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THE EDITORS.

ON THE PRODUCTION OF X-RADIATION, ACCORDING TO WAVE MECHANICS.

BY

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As early as twenty years ago, I gave[1] an account of the production of general X-radiation from the standpoint of the classical theory. The quantum theory had not been developed sufficiently at that time and was not, in any case, sufficiently familiar to myself. The assumption was made that the cathode particles impinging on the target became retarded in a rectilinear manner, so as to prolong the direction of the incident beam by a finite distance OO' into the target; comp. Fig. 1. The electromagnetic radiation emitted by this process of stoppage is given by the formula

$$(1) \qquad E = H = \frac{e\dot{v}}{c^2 r} \frac{\sin \theta}{(1 - \beta \cos \theta)^3},$$

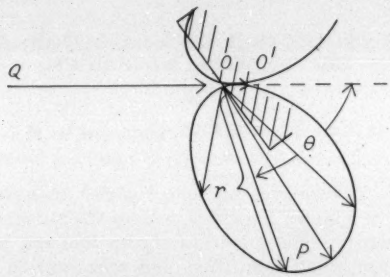
r being the distance from the target O to the point P where the X-ray is observed and θ, the angle between the incident

[1] A. Sommerfeld, as a colleague of the late Professor Roentgen, *Physikal. Zeitsch.*, 10, p. 969, 1909.

cathode beam QOO' and the direction, OP, of the X-ray. $\beta = v/c$ is the ratio of the velocity of the cathode particle in any special phase of the stopping process to the velocity of light, $-\dot{v}$ is the "deceleration" of the electron, which was taken as uniform during the stoppage. The intensity of X-radiation to be observed at the point P was derived by an integration with respect to B.

At the time of the foregoing investigation, the spectral revolution of X-rays was, of course, unknown. Therefore, the intensity formula given above refers to the total intensity contained in the continuous spectrum. The characteristic or line spectrum was not treated in my former note and will not be considered in the present paper.

FIG. 1.



Formula (1) provides for polarization of the general X-radiation of the same character as that shown by the earlier experiments of Barkla and others. Moreover, it shows immediately that the maximum of emitted intensity is not to be found for the angle $\theta = \pi/2$, as would be expected from the numerator $\sin\theta$ alone, but should be shifted to smaller angles, because of the denominator. This shift, which is shown qualitatively in Fig. 1, increases with the value of β, that is with increasing voltage of the impinging cathode rays. It turned out to be in general agreement with simultaneous observations of I. Stark and with later more accurate observations undertaken for the special purpose of testing my formula for angular intensity distribution.

Today one has to attack the same problem by using the methods of wave mechanics instead of classical methods, and one has to compute the specific intensity in any range of the continuous spectrum instead of the total intensity emitted in the general radiation. Moreover, one is interested mainly, not in the emission of a thick target, in which processes of uncontrollable character go on, such as diffusion and multiple scattering, but in the emission of a single atom or even a single nucleus, which can be defined unambiguously by wave mechanical methods. Such an emission is accomplished by the experiments of W. Duane [2] with mercury vapour, by the experiments of D. L. Webster,[3] with thin foils of silver overlying a thick platinum target, and, particularly by the careful observations of H. Kulenkampff [4] with very thin aluminum foils.

When I crossed the Pacific, I tried to account for the angular distribution of intensity in the experiments of Kulenkampff and to understand the difference between these and the former experiments with thick anti-cathodes. This task has turned out to be rather a long one. I shall report here the first steps in this direction; the main discussion of Kulenkampff's angular distribution of X-radiation is given in a paper presented to the National Academy of America, which is now in print, so that I shall allude here to this question only briefly.

1. FORCED AND FREE OSCILLATIONS IN AN ACOUSTICAL RESONATOR.

In the Loomis Laboratory it may be not out of place to start with a typical problem in acoustics. Fig. 2 shows an acoustical resonator with a finite boundary, the boundary condition being e.g. $x = 0$. There is an infinite number of free oscillations continuous throughout the inside satisfying the condition on the boundary. These free oscillations may be called ψ_r, the corresponding frequencies (wave numbers) K_r. The differential equation connecting both is

$$\Delta\psi_r + K_r^2\psi_r = 0. \tag{2}$$

[2] W. Duane, *Proc. Nat. Ac.*, 13, p. 662, 1927; 14, p. 450, 1928.
[3] D. L. Webster, A. Clark, etc., *Proc. Nat. Ac.*, 14, p. 679, 1928.
[4] H. Kulenkampff, *Ann. d. Phys.*, 87, p. 597, 1928.

The ψ_r and K_r constitute the system of "eigenfunctions" and "eigenvalues" characteristic for our boundary problem. We seek for the forced oscillation ψ, excited by a certain unit source Q, pulsating with a given wave number K different from all the K_r's. The differential equation defining this forced oscillation is

$$\Delta\psi + K^2\psi = \begin{cases} 0 \\ \infty \end{cases}, \tag{3}$$

the right side being 0 for all points P different from Q, but ∞ for $P = Q$. The point O, which is marked in Fig. 2, also, may be disregarded at present. It can be easily shown, that the problem proposed can be expressed in terms of the free oscillations by the following formula

$$\psi = \sum_r \frac{\psi_r^*(Q)\psi_r(P)}{K^2 - K_r^2}. \tag{4}$$

The functions ψ are supposed to be normalized in the ordinary way so that

$$\int \psi_r \psi_r^*(Q) dI = 1, \tag{5}$$

ψ_r^* meaning the conjugate complex to ψ_r, if ψ_r is not real. The integral is to be taken over the whole inside of our boundary; the same holds for all the following integrals. Formula (4) is known from the theory of integral equations. I have proved it [5] in a much less rigorous way by the following reasoning:

Replace the right side of (3) by a continuous distribution f of sources of such a character, that f becomes very small for $P \neq Q$ and takes very high values in the neighbourhood of $P = Q$. What we have called "unit source" is secured by the condition

$$\int f d\tau = 1. \tag{6}$$

We develop f in a series of "eigenfunctions" ψ_r:

$$f = \sum A_r \psi_r. \tag{7a}$$

[5] A. Sommerfeld, Jahresbericht der deutschen Mathematiker-Vereinigung, 1912. Über die Greensche Funktion der Schwingungs-gleichung. The function introduced here is an anticipation of Dirac's function Δ.

In the same way we develop the unknown functions ψ;

$$\psi = \Sigma B_r \psi_r. \tag{7b}$$

Introduction (7a) on the right, (7b) on the left of equ. (3) and using (2), we get from the comparison of the coefficient of ψ_r on the left and right:

$$B_r = \frac{A_r}{K^2 - K_r^2}.$$

As is computed from (7a) in Fourier's manner. With regard to the normalization condition (5) and to the orthogonality of the ψ_r one gets

$$A_r = \int f \psi_r^* d\tau.$$

But f is different from zero only in the neighbourhood of Q. So we may write $\psi_r^*(Q)$ instead of ψ_r^* and put it out of the integral sign. Using (6) we see

$$A_r = \psi_r^*(Q) \int f d\tau = \psi_r^*(Q), \quad B_r = \frac{\psi_r^*(Q)}{K^2 - K_r^2}.$$

This value of B_r together with the expansion (7*b*) proves the proposed formula (4). The system of " eigenfunctions " is of course to be supposed as complete in order that the expansions (7a, b) are possible.

The main point in my former paper [5] has been the transition to the limit of an infinite region. Then the discrete spectrum of the free oscillations becomes continuous. Introducing polar coördinates r, ϑ, φ with the centre O (Fig. 2), we call ρ the parameter of the continuous spectrum corresponding to the radius vector r; l and m are integral numbers or ' quantum numbers,' describing the angular dependence of the eigenfunctions on the variables ϑ and φ. It is evident that the spectrum becomes continuous only in the parameter ρ, because only r goes to infinity; with respect to l and m the spectrum is discontinuous as before, because ϑ and φ are restricted to the finite limits $0 < \vartheta < \pi$, $0 < \varphi < 2\pi$. Instead of ψ_r we now have to write explicitly $\psi_{\rho lm}$ and equation 4 takes the form

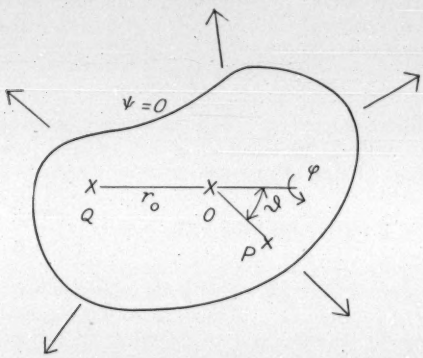
$$\psi = \int_0^\infty \sum_{lm} \frac{\psi_{\rho lm}^*(Q)\psi_{\rho lm}(P)}{K^2 - \rho^2}. \tag{8}$$

It is well known, that in the simple acoustical case one has besides the necessary normalizing factors:

$$\psi_{\rho lm}(P) = X_l(\rho r) P_l^m(\cos\vartheta) \begin{matrix}\cos \\ \sin\end{matrix} m\varphi.$$

Here X_l is the Bessel function $J_{l+\frac{1}{2}}$ divided by the square root of the argument (ρr), P_l^m is the so-called associated spherical

FIG. 2.



harmonic. In the same way, if r_0, ϑ_0, ϕ_0 are polar coördinates of the point Q,

$$\psi_{\rho lm}(Q) = X_l(\rho r_0) P_l^m(\cos\vartheta_0) \begin{matrix}\cos \\ \sin\end{matrix} m\phi_0.$$

If, in particular, we put $\vartheta_0 = \pi$ (Fig. 2) all the P_l^m vanish except $m = 0$ and equ. (8) takes the simpler form:

$$\psi = \int_0^\infty d\rho \sum_l \frac{X_l(\rho r_0) X_l(\rho r)}{K^2 - \rho^2} P_l(-1) P_l(\cos\vartheta). \tag{9}$$

As shown in the former paper [5] the integration over ρ can be carried out. Here the boundary condition for infinite distance becomes essential ("Ausstrahlungs—Bedingung"). We have to postulate, that ψ is represented by a

system of *divergent* waves; *convergent* waves coming from infinity are excluded by the physical meaning of our problem. This condition of divergent waves can be fulfilled in a very remarkable and simple manner: The path of integration from O to infinity in the ρ plane is to be traced so, that it runs not along the real axis but in the negative imaginary half of the complex plane, the singularity $\rho = K$ on the left side. Then the integration can be reduced in Cauchy's manner to a circuit around the point $\rho = K$. But it is necessary before doing that to split up the function X_l in two parts (we suppose $r_0 > r$ and put $u = \rho r_0$):

$$X_l(u) = \tfrac{1}{2}\{X_l^1(u) + X_l^2(u)\}, \tag{10}$$

which formula corresponds exactly to the well known relation between Bessel function of any index and both Hankel functions H^1 and H^2,

$$J(u) = \tfrac{1}{2}\{H^1(u) + H^2(u)\}.$$

Introducing (10) in (9) and carrying out the integration, we get

$$\psi = \frac{\pi i}{2K}\sum_l X_l^1(Kr_0)X_l(Kr)P_l(-1)P_l(\cos\vartheta), \tag{11}$$

observing that the part X_l^2 in (10) does not contribute to the integral because it vanishes in the negative half of the complex ρ plane.

Equ. (11) is nothing other than the expansion of the simple expression

$$\psi = \frac{e^{ikR}}{R} \tag{12}$$

in spherical harmonies where R is the distance PQ, viz. $R^2 = r^2 + r_0^2 + 2rr_0\cos\vartheta$. Indeed the forced oscillations in our acoustical problems, emitted from the source Q, are described by the function (12) of the spherical wave, equ. (11) expressing the so-called addition theorem of this function.

The last step we have to make in connection with the acoustical problem is the transition to the limit $Q \to \infty$, $r_0 \to \infty$. Then the spherical wave (12) turns out to be the

plane wave e^{iKr}, and the expansion (11) is transformed into the well known form

$$e^{iKr} = \sum_{l=0}^{\infty} (2l + 1) i^l X_l(Kr) P_l(\cos\theta), \tag{13}$$

the factor i^l resulting from the limiting value of $X_l'(Kr_0)$ for $r_0 \to \infty$ and the factor $(2l + 1)$ from the usual normalization of $P_l(\cos\vartheta)$.

2. DIFFRACTION OF AN ELECTRONIC WAVE BY A SINGLE NUCLEUS.

The problem of diffraction of a beam of electrons by an atom has been treated until now only by the method of perturbations. We propose to solve it here by an exact formula, which may be more suitable, even in complicated cases, than the step by step method of perturbations. At present we restrict ourselves to the simplest case of a bare nucleus, in which the formulæ we arrive at are not new.

For the first place we have to show that our general formula (4) holds in this case. It is true that the acoustical differential equation (2) is to be changed in the wave mechanical equation

$$\Delta\psi_r + K_r^2\psi_r = 0, \quad K_r^2 = \frac{8\pi^2 m}{h^2}(E_r - V), \tag{14}$$

where in the case of a bare nucleus of charge $+ Ze$,

$$-V = \frac{Ze^2}{r}.$$

In this way our differential equation has no longer constant coefficients K_r depending on the distance $r = OP$ (O being the position of the nucleus, P the point of reference). We write

$$K_r^2 = k_r^2 + \frac{A}{r}, \quad k_r^2 = \frac{8\pi^2 m}{h^2} E_r, \quad A = \frac{8\pi^2 m}{h^2} Ze^2, \tag{15a}$$

and in the same way

$$K^2 = k^2 + \frac{A}{r}, \quad k^2 = \frac{8\pi^2 m}{h^2} E. \tag{15b}$$

Here E means the energy of the electrons emerging from

the source Q, that is the kinetic energy $mv^2/2$. Therefore k^2 turns out to be

$$k^2 = \left(\frac{2\pi mv}{h}\right)^2 = \left(\frac{2\pi}{\lambda}\right)^2$$

if we define λ by deBroglie's formula, so that in this case also, k can be called the wave number of the electron beam.

The equation to be integrated in the diffraction problem originates from (14) by omitting the indices r and substituting for the right side the distribution function f defined in Sec. 1, and alluded to in equ. (3). Now we have only to remark that according to (15a, b) the quantity

$$K^2 - K_r^2 = k^2 - k_r^2$$

becomes independent of r, to see that the whole procedure of Sec. 1, can be used without change even in the present case. The only difference is, that the eigenfunctions ψ_r are not the acoustical ones, but are defined by the more complicated differential equation (14) together with the condition on the boundary. These functions are unknown; but if we remove the boundary to infinity, the ψ_r become identical with the eigenfunctions of the simple Kepler problem. The spectrum of the corresponding eigenvalues is known to be partly continuous, partly discrete.

For the continuous part of the spectrum we may use directly equ. (8), changing of course the meaning of the functions $\psi_{\rho lm}$. The discontinuous part of the spectrum gives rise to an equivalent expression in which the integration is replaced by a summation. But this expression will vanish exponentially if we go to the limit $Q \to \infty$ because of the well known properties of the discontinuous eigenfunctions in the Kepler problem. So we may omit this expression even now. As long as Q is a point at a finite distance from O, we deal with an electron stream emerging from a thermionic point source; if we remove Q to infinity we pass to a parallel electron stream, that is a plane electron wave.

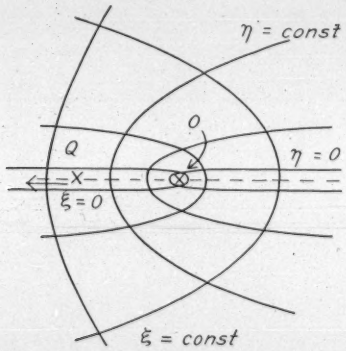
There is no difference in the method of integration leading from (9) to (11), the radial functions X_l and X_l' being now definite solutions of the differential equation of the Kepler problem. The formula (13) for the plane wave is to be re-

written now in the following way

$$\psi = \sum_l (2l + 1) i^l e^{i\sigma_l} X_l(k, r) P_l(\cos \vartheta). \tag{16}$$

The left hand side is of course no longer the undisturbed plane wave e^{ikz}, the original plane wave being diffracted or scattered by the field around the nucleus. The exact amount of scattering is to be derived from the right hand side of (16), which defines ψ for each direction ϑ and for each distance r from the nucleus. The X_l are derivatives of the Laguerre functions for a certain level in the continuous spectrum

FIG. 3.



specified by the wave number K. The factor $e^{i\sigma_l}$ by which (16) differs from (13), originates in the asymptotic expression of the corresponding Laguerre functions for the point Q in the limit $Q \to \infty$.

Equ. (16) is derived by W. Gordon [6] in a somewhat different way and is used by him to show that it conforms with Rutherford's formula for the scattering of particles by a nucleus.

Until now we have used polar coördinates r, ϑ, φ. But it can be seen, that the parabolic coördinates ξ, η, φ, known from the quantum theory of the Stark effect, are better

[6] W. Gordon, *ZS. f. Phys.*, 48, p. 180, 1928.

adapted to our diffraction problem. This was stated first by G. Temple [7] who proceeded in this way to a very simple wave mechanical derivation of Rutherford's formula. Indeed the symmetry of our diffraction problem with an electronic wave propagated in the positive x-direction (Fig. 3) is similar to the symmetry of the Stark effect with a homogeneous electric field parallel to the positive x-axis. The eigenfunctions in parabolic coördinates have the general form, known from the Stark effect:

$$\psi = f_1(\xi) f_2(\eta) \begin{matrix}\cos \\ \sin\end{matrix} m\varphi.$$

But, because of the symmetry around the x-axis, only those functions are to be used which are independent of φ, so that we have to put $m = 0$. For the continuous spectrum the expression of f_1, or f_2 for $m = 0$ may be written in the usual form.

$$f(u) = e^{\pm iu/2} L(u), \quad u = k\xi \text{ or } k\eta. \tag{17}$$

Here k is the wave number of the incident electron beam, corresponding to a definite level E of the continuous spectrum according to the formulæ:

$$k = \frac{2\pi}{\lambda} = \frac{2\pi}{h} mv = \sqrt{\frac{8\pi^2 m}{h^2} E}.$$

L is a solution of the differential equation of Laguerre, not a polynomial but an holomorphic transcendental function. L is represented by a complex integral, the path of integration enclosing two branch points. This path can be transformed into two loops, each of which starts from infinity, goes around one of the branch points and ends in infinity. In this way L is split up in two parts L^1 and L^2, which generally have a singularity for zero argument. The point L^1 is to be used in the analogue to formula (11) instead of $X_i'(Kr_0)$, relating to the source point Q. We put the point Q on the degenerated parabola $\xi = 0$ comp. Fig. 3. But then our general representation would break down, because $L^1(0)$ is singular, not only at the point Q but along the whole parabola $\xi = 0$. We would not have a source point but a source line. There-

[7] G. Temple, *Proc. R. Soc.*, 121, p. 673, 1928.

fore we have to look for such a special solution $L'(\xi)$ of the differential equation, as does not become infinite for $\xi = 0$. The only solution of this type is $L'(\xi) = \text{Const.}$; it occurs only for a special choice of the parameter n, contained in the differential equation. This parameter, which is equivalent to the degree n of the Laguerre polynomials in the discreet spectrum, is determined in this way uniquely. It holds not only for the factor $\psi(Q)$ of our general solution, but also for $\psi(P)$. The conclusion drawn from this amounts to the following; that the analogue to the sum (11) consists in the case of parabolic coördinates of one member only. The part depending on ξ is simply (fr. (17))

$$f_1(\xi) = e^{ik(\xi/2)} \cdot \text{Const.}$$

the part depending on η may be written:

$$f_2(\eta) = e^{-ik(\eta/2)} \cdot L(k\eta).$$

L being the holomorphic solution of the Laguerre differential equation in η for the same parameter n; this solution in η is not a constant. In the limit $Q \to \infty$ we get as a representation of an incident plane wave scattered by a nucleus at the point O;

$$\psi = e^{i(\xi/2)} \cdot e^{-ik(\eta/2)} \cdot L(\eta). \tag{18}$$

The constant part corresponding to the factor $\psi'(Q)$ is omitted here.

Because of the relations betweens parobolic and rectangular coördinates

$$x = \frac{\xi - \eta}{2}, \quad r = \sqrt{x^2 + y^2 + z^2} = \frac{\xi + \eta}{2},$$

we may write for (18):

$$\psi = e^{ikz} L(k\eta) = e^{ikz} L[k(r - x)]. \tag{19}$$

This very simple result shows immediately how the incident wave e^{ikz} is modified by the scattering or diffraction factor L.

3. SOME GENERALIZATIONS.

In the foregoing we have discussed what may be called *elastic* scattering by a bare nucleus. In this case we deal

with a *one-electron-problem*, characterized by the occurrence of the *Hydrogen-eigenfunctions*. Concerning inelastic scattering, we have to suppose a nucleus with surrounding electrons, bound by the nucleus, because the bare nucleus cannot take up energy. It is understood that we ascribe to the nucleus in any case an infinite mass so that we need not care for the conservation of momentum.

In the first place we will speak about the *elastic scattering* by *neutral Hydrogen*. In this case we deal with a *Two-electron problem*, one electron impinging and one electron bound. So we have not a problem of three degrees of freedom (three coördinates) as before, but of six. The characteristic eigenfunctions are now those of *Helium*, of course not of an ordinary Helium atom with double nuclear charge, but only with one nuclear charge. The possibility of the interchange between the impinging and the bound electron is indicated by the formal structure of the Helium-eigenfunctions. But the general procedure remains the same as in the case of a bare nucleus: the exact solution of our present diffraction is built up by those Helium-eigenfunctions in the same way as it has been in the former case by the Hydrogen-eigenfunctions. As to the finding of the amount of scattering in the ordinary space, we have to integrate our six-dimensional formula with respect to the three coördinates of the bound electron. The difficulty resides only in the more complicated nature of the eigenfunctions now to be used.

In the same way we have to introduce the Lithium atom with nuclear charge 2 if we ask for the scattering of a Helium atom. It is significant that correspondingly the scattering problem by rare gases is governed by the rather simple spectral functions of the alkali atoms. The Ramsauer effect, which is shown in the simplest form by atoms of the rare gases, is of course the limit of the scattering problem for $v = 0$, v meaning the velocity of the impinging electron. I should like to suggest that the characteristic features of the Ramsauer effect in rare gases may be connected with the especially simple structure of the Alkaline spectra.

We have treated the elastic collision as a stationary state, in which neither the atom nor the character of the incident wave is ever changed. We propose to treat also the inelastic

collision as a stationary state, differing from the elastic collision only in that we have here the atom in an excited state. The amount of scattering for any direction can be derived from this stationary state in the same way as from the stationary state corresponding to an elastic collision.

By this method we are not informed at all concerning the radiation as a consequence of inelastic collisions. As to the radiation problem we must compare the initial state of things (Energy $E_1 = (m/2)v_1^2$ of the impinging electron; energy level E_1 of the atom) and the final state (Energy $E_2 = (m/2)v_2^2$ of the electron, reduced by the inelastic collision; Energy $E_2 \geq E_1$ of the atom after radiation); the intermediate state (Energy E_2 of the electron and energy level $E_3 > E_2$ of the atom) not coming into consideration and perhaps not being realized in nature. In this way one can hope to get a simple mathematical definition of what is called the *excitation unction* of a certain spectral line by electron impact, in the case of visible light, as well as in the case of characteristic X-radiation. The scheme to be followed in the mathematical treatment will be shown in the next paragraph dealing with the excitation of the continuous spectrum of X-radiation.

4. PRODUCTION OF X-RAYS.

We will consider a bare nucleus of atomic number F and treat the impinging cathode ray as a stationary wave, proceeding in the direction of the positive axis of x with a wave number k (velocity v_1). The behaviour of this wave under the influence of the nucleus is described by formula (19), which we may rewrite at present:

$$\psi_1 = z^{ik_1 x} L(k_1 \eta). \tag{20}$$

Because of the stationary character of the incident wave the time dependence is harmonic and given by the total energy of the electron at infinite distance from the nucleus, viz.:

$$E_1 = mc^2 + \frac{m}{2} v_1^2.$$

The relativity correction is omitted here for the sake of brevity. The complete representation of the wave function

with regard to space and time will be, consequently,

$$\Psi_1 = \psi_1 e^{(2\pi i/h)E_1 t} = e^{ik_1 x} L(k_1\eta) e^{(2\pi i/h)E_1 t}. \tag{21}$$

The collision of the electron with the nucleus is an inelastic one, the velocity v_1 being reduced to v_2. The corresponding wave number and energy of the emergent electron are k_2 and

$$E_2 = mc^2 + \frac{m}{2} v_2^2.$$

If we assume that the electron *conserves its direction of motion* (in which case the recoil of the nucleus would be in the direction of the positive x-axis), the wave function for the emergent electron will be

$$\Psi_2 = \psi_2 e^{(2\pi i/h)E_2 t}, \quad \psi_2 = e^{ik_2 x} L(k_2\eta). \tag{22}$$

We seek the X-radiation connected with this inelastic collision. We calculate it in the manner used in the usual treatment of intensity questions in line spectra. Starting with the combined density ρ_{12} of the initial and the final state

$$\rho_{12} = \Psi_1 \Psi_2^*$$

we form the moment M of this density for any coördinate g; the so-called " matrix element ":

$$M = \int g\rho_{12} d\tau = \int g\psi_1 \Psi_2^* d\tau \cdot e^{i\omega t}, \tag{23}$$

where

$$\omega = \frac{2\pi}{h}(E_1 - E_2) = \frac{2\pi}{h} \cdot \frac{m}{2}(v_1^2 - v_2^2) \tag{24}$$

is the frequency of radiation belonging to a certain element of the continuous X-ray spectrum. The field emitted is proportional to $\ddot{M}$ in agreement with equ. (1) in which $\ddot{M}$ is represented by the more specialized factor $e\dot{v}$. The amount of radiation becomes in this way proportional to $[\ddot{M}]^2$, containing therefore the well known factor ω^2. As to the direction Θ the radiation is proportional to the expression (cfr. equ. (1)):

$$I = \frac{\sin^2 \theta}{(1 - \beta \cos \Theta)^6}, \tag{25}$$

which represents *the angular distribution of intensity* in the special case in which the emergent electron follows the direction of the incident electron. Here the velocity ratio β i.e., v/c, is to be assigned. Considering that the denominator in (25) is somewhat like a Doppler effect and originates in the relative motion of the source of radiation with respect to the observer, who is supposed to be at infinite distance in the direction Θ it is natural to define this relative motion by the arithmetical mean

$$v = \tfrac{1}{2}(v_1 + v_2).$$

Thus we get:

$$\beta = \frac{v}{c} = \frac{v_1 + v_2}{2c}. \tag{26}$$

I have compared [8] equ. (25) with the results of *Kulenkampff*, mentioned in the introduction, and have found a very good agreement as to the position of maximum emission. It is not necessary to repeat here the discussion. I wish only to emphasize one significant point. The shift of the maximum in the direction of the incident wave increases, according to (25), with the increasing β. For the continuous spectrum for a given voltage (given v) β increases with increasing v_2. But increasing v_2 means, according to (24), decreasing frequency, that is decreasing hardness of the X-radiation. Thus we get a result, at first sight paradoxical, i.e., the shift of the maximum increasing from the short wave-length limit ($v_2 = 0$) towards the softer part of the continuous spectrum. This result agrees very nicely with the observations of Kulenkampff not only in a qualitative but also in a quantitative way.

Our assumption as to the direction of the emergent electron provides complete polarization of the emitted radiation. Indeed from equ. (23) it is seen immediately that only the x-component of M will be different from zero, while the components $g = y$ and $g = z$ vanish because of the symmetry of our integral. It is true that we have to introduce in equ. (23) a retardation phase factor corresponding to the wave proceeding in the direction θ by which the original

[8] G. A. Ross, *T. of the Optical Soc. of Amer.*, 16, 375, 1928.

symmetry of the integral is somewhat altered. This retardation rests on the fact, that our charge distribution ρ_{12} is not at all a point charge, as it would be approximately in the case of line emission in the discontinuous spectrum, but extends over the whole space. But for observations under right angle to the incident beam ($\theta = \pi/2$) the polarization will be complete, according to our previous formula, even if retardation is taken into account. This consequence seems to be in contradiction to the observations available for Mercury vapour of W. Duane and seems to be right only for the short wave-length limit of the continuous spectrum.[8]

There is another point in which the observations seem to contradict our theoretical expectation. If the moment M has only the one component M_x, there would be no radiation in the direction of X, that is for $\Theta = 0$ and for $\Theta = K$. But according to Kulenkampff [4] that is true only close to the limit of the continuous spectrum. For other parts of the spectrum the curves communicated by Kulenkampff point to a certain amount of radiation emitted in both directions $\Theta = 0$ and $\Theta = \pi/2$. The same conclusion has been drawn by W. Duane from his observations with Mercury vapour, as communicated in the discussion of this paper in the Loomis conference.

I am indebted deeply to Prof. E. C. Kemble for having suggested to me in the same discussion a generalization of my original assumption by which the contradictions mentioned above may be avoided. The generalization is to admit secondary beams emergent from the scattering nucleus *in any direction* not only in the direction of the incident beam. This amounts to averaging ψ_2 in the matrix element M over all possible angles, in other words, to substituting in equ. (23) for ψ_2

$$(27) \qquad \bar{\psi}_2 = \frac{1}{4\pi}\int \psi_2 d\omega, \quad d\omega = \sin\vartheta' d\vartheta' \cdot d\varphi',$$

where the angles ϑ' and φ' indicate the direction of the emergent beam. I am also indebted to Prof. Kennard for having emphasized in the same discussion the analogy of this procedure with the usual treatment in the case of line spectra. Calculating the intensity of spectral lines we have to sum up

the matrix element over all the different orientations of the atom, characterized by the magnetic quantum number m and belonging to the same energy level. This summation over m corresponds to our present integration over $d\omega$. For the same way that we calculate in line spectra each orientation with the weight one, we have given in our formula (27) the same weight to each direction of the emergent beam.

According to our present assumption, the polarization will be complete only for zero velocity of the emergent beam, i.e., only for the short wave-length limit of the continuous spectrum, because in this case we will have

$$\bar{\psi}_2 = \psi_2 = 1.$$

Only in this case will there be no radiation emitted in the direction $\Theta = 0$ and $\Theta = \pi$ of the incident beam. In all other cases, $v_2 > 0$, i.e. for other regions in the continuous spectrum the polarization will be incomplete and the radiation for $\Theta = 0$ and $\Theta = \pi$ will not vanish because of the emergent beams forming an angle with the incident beam. These conclusions are in a general agreement with the observations of Duane, Ross, Kulenkampff, mentioned before.

In conclusion, I should like to state that the exact computation of the matrix element M meets with some convergency difficulties which I have not overcome as yet. Also the question of elastic and inelastic collisions with real atoms containing one or more electrons needs more detailed considerations as to the nature of the eigenfunctions therein required. But I think that, by the method here described, a new and promising way is opened for many interesting problems related to electron impact.

THE EXCITATION OF THE SPECTRUM.

BY

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THE main problem treated by intensity measurement was that of the determination of the emission probabilities for given atomic levels. The investigations which led to the sum rule, the multiple intensity rules, the intensities of Zeeman effects and the intensity regularities in band spectra belong all to this category.

Now another problem is certainly of even greater interest —how can the energy distribution of the lines of a spectrum be accounted for? If we know the transition probabilities, we want knowledge of the number of atoms on the different levels in order to solve that problem. The problem is in many respects more complicated as the same level can be originated by very different types of excitation. So for example the excitation can be caused by the absorption of radiation as well from the fundamental level—the most common case—as from excited levels. Generally, a good measurement of absorption is very difficult and is only possible with apparatus of great dispersion. We know however some rules about the coefficients of absorption; and a well-known relation exists between the coefficients of absorption and emission given by Einstein in his deduction of Planck's law from the Bohr atomic model, therefore absorption measurement can often be replaced by the much simpler measurement of emission. One of the rules on absorption is that absorption of radiation is only possible if the initial and final states differ by unity in the azimuthal quantum number.

The alkali vapours at low temperatures absorb only the lines of the principal series for the initial level is an s level while the final state has a p level (k changing therefore from $1/2$ to $3/2$). At the higher temperature of an excited state, the lines of the other series can be absorbed.

A like law holds for the absorption in helium. The fundamental level is an $'S$ level and there only $'P'S$ lines can be absorbed. For other elements with singlet-triplet systems this rule does not hold, there is also as well in emission, as in absorption, an intercombination line of emission and absorption which generally is much weaker than the corresponding singlet absorption line. Phenomena of this kind play a part in the equilibrium of radiation and atoms, and are of great importance for astrophysics. Another action of the radiation presents itself in the Raman effect, where not the whole quantum is used to bring an atom or molecular system to a higher state but only a part, the rest being emitted as radiation of lower frequency, or in other cases an excited system loses its energy which is added to the energy of the impinging light quantum. The study of this phenomenon with the help of intensity measurement can give a test of the Maxwell-Boltzmann distribution law.[1]

Now there are two other ways of excitation by which an atom can be brought to another state, i.e. by the collision with electrons, or with neutral or excited atoms. When we study the spectrum produced in a Geisler tube or in an arc we find that both the types of excitation take place. I thought that it would be interesting to dwell somewhat longer on a series of experiments which are now being carried on in the Utrecht Institute on helium from which some general conclusions on electronic excitation can be drawn. The helium spectrum is investigated in Geisler tubes with different pressures, with or without glow cathode, under constant tension (varying from 400 to 1500 v.), for low pressure tubes with an equipotential cathode are used with a grid parallel to the cathode through which the electrons enter with varied velocities into a field free space. The stronger lines are measured with monochromator and thermocouple joined to a Moll-Burger thermogalvanometer combination, the weaker lines are measured with the Utrecht photographical photometric method. Often, at low pressure and low electron velocity, exposures of 48 hours' duration are used if it is necessary.

[1] Comp. a publication of L. S. Ornstein and Rekveld finished since (*Phys. Rev.*, 1929).

The first problem which was investigated in the work of Burger and myself was that of the equilibrium of the 2^3P and of the $2'P$ levels.

From these levels the $2^3S - 2^3P$ and $2'S - 2'P$ lines originate and the lines of the $2^3P - m^3S$ and $2^3P - m^3D$ series (sharp and diffuse series) bring other atoms to the 2^3P state and analogously in the singlet system. Now we have measured the number of jumps to and from the 2^3P and $2'P$ levels as a function of the pressure, with the result that even at our lowest pressure (0.01 mm.) the atoms coming down to the P levels are a small fraction of those starting from those levels (in the maximum ratio at the lowest pressure). From this fact we can conclude that the excitation of the ^2P level takes place chiefly from the lower states and that the idea that the atoms are ionized and the spectrum is formed by successive forming of atoms in excited states (ionization spectrum) is not true for our case. Measurements performed on the resonance lines of the alkalies and of the lines of the sharp and diffuse series for the case of arcs show that also for this kind of excitation direct excitation of the $^2p_1$ and $^2p_2$ levels are the principal cause of the D line emission. The same is the case for the flame excitation of alkalies and perhaps this is the reason that the D lines are present to an intensity corresponding to black body temperature radiation of the flame temperature as the lines of the sharp and diffuse series being present at the same time with an intensity corresponding to a much higher temperature. In order to understand this fact one has to bear in mind that the p levels are excited by the black body radiation in the flame as the higher levels may be attributed to chemical reactions.[2]

Further facts can be found if we investigate the ratio of the corresponding singlet and triplet lines as a function of the pressure. When the levels are occupied proportional to the statistical weights the ratio of line intensities (divided by the fourth power of the frequency) ought to be 1 : 3. Now for corresponding pd, sp and ps lines this ratio has been determined as a function of the pressure. At low pressure the singlet lines are relatively much too strong, at higher

[2] Comp. Miss C. E. Blecker, Faraday Transactions 19. Symposium on photochemistry.

pressures the ratio becomes larger and gets the normal value only for the pd lines. From this fact we can conclude something about the excitation if we bear in mind that at low pressure the collisions between excited and unexcited atoms are rare, so that we find at low pressure the true result of excitation. The result therefore is that the singlet levels are more readily excited by electron impact than the triplet levels. This fact is in correspondence with the properties of helium when excited by radiation; for radiation, the transition singlet-triplet seems to be forbidden; for electronic actions, we cannot say that this transition is forbidden but it is much more rare than the corresponding transition singlet-singlet. The fact that the ratio for $p - d$ becomes normal and for $s - p$ and $p - s$ is far above the normal is also very interesting. When we look at the term scheme of helium, we find that the difference of the corresponding $'d$ and ^3d levels is of the order of the energy of translation of the molecular motion, for p and s levels however the difference is much larger. Therefore for the d levels, we find that the transitions $'d \rightarrow {}^3d$ and $^3d \rightarrow 'd$ are possible so that by molecular impacts the equilibrium as given by the statistical weight can come into existence at higher pressures where the number of impacts is large; however, the $'s \rightarrow {}^3s$ and $'p \rightarrow {}^3p$ transitions being possible, the $^3s \rightarrow 's$ and $^3s \rightarrow 'p$ transitions cannot occur, the thermal energy being too small to provide the necessary amount of energy. Our conclusion is therefore that for electron impacts there is a preference for the formation of singlets, with the atomic impacts on the other hand each transition which is possible from the point of view of the energy required will occur.

The analogy of the action of radiation and electrons for the triplet-singlet suggest that there ought to be an analogous fact for the ^3p levels in the singlet system. For as we have mentioned already, the fundamental level for helium is an $'s$ level, and therefore the absorption of light is only possible for the $'p - 's$ radiation when the helium is in the unexcited state. The experiment confirms this expectation. When we measure the green line (5016) $(2's - 3'p)$ which is an $'s - 'p$ line as a function of pressure and compare this line with the $'p - 'd$ and $'p - 's$ lines, we find that at low pressure the

relative intensity of the green line is much stronger than at higher pressures. The same is true for the 3965 ($2's - 4'p$) line. It seems also therefore that the change of azimuthal quantum number by electronic impact shows a striking analogy with the effect of radiation.

Before I give a discussion of further experiments on helium it is perhaps good to apply this result to the problem of the hydrogen fine structure. In most of the experiments on the doublets of $H_\alpha H_\beta$ the proportion of the intensities of the components is not in accordance with the calculations of quantum mechanics. Only at fairly high pressures and current densities the theoretical laws seem to hold. Now it is generally adopted that results at high pressures and current densities are farther from the theoretical values by self-absorption. In our case however the question is another one —The experiments of Snoch described in his dissertation (Utrecht, 1929) show that as a function of the current the doublet intensities approach with larger currents to the theoretical limit, therefore it seems that at the lower limit there is something deviating from the theoretical conditions and this can be the way in which, at such pressures, the levels are occupied. The level from which H_α and H_β' originate are combinations of *spd*, *spdf* levels, the fundamental level of the hydrogen atom is an *s* level, therefore at low pressure there will be a much stronger occupation of the *p* than of the other levels, the deviations of the theoretical values are in this sense.

In further experimental work on helium the excitation was studied for electrons of known velocity and at different pressures. When we plot the intensity of the lines as function of the voltage between the grid and the glow cathode we get for all the lines, curves which show one or more maxima. The curve for lines 5016 and 3965 ($2'S - 3'P$, $2'S - 4'P$) have been followed to about 30 v. and show a tendency to strike the axis at the potential necessary for the $'p$ levels from the $'s$ level, which is in accordance with the result found from the fact that these lines get stronger at low pressure as all the other singlet lines do.

The triplet-singlet ratios have been measured between 30 and 80 volts; they show maxima and fall to zero at very

low velocity. The ratio $\frac{2^3P - 4^3S}{2'P - 4'S}$ has two maxima at 35 and 63 v. The difference is of the order of the ionization voltage, the second maximum can therefore be a repetition of the first caused by electrons which have first ionized and kept enough energy to excite other atoms.

The $\frac{2^3S - 3^3P}{2'S - 3'P}$ ratio has a maximum at about 40 v.; this might be described in the following way: When this proportion is large, $2^3S - 3^3P$ (3889) must be strong. The atoms on the 3^3P line can be formed by electronic impact from the metastable, 2^3S, level, which can be formed at 20 v. We should therefore find maxima also, 40 and 60 v; at 30 v. the curve intensity voltage is still going ahead.

The polarization of the He lines has been measured. It is larger for triplet than for singlet lines and also larger for the higher numbers of a series.

I hope that the facts exposed in this lecture show how important the intensity measurement of excitation is for the development of theory, as it seems. I refer to the work of Oppenheimer—that a theoretical calculation of many phenomena for simple atoms belongs to the possibilities of the mathematicians.

The work described here has been partly worked out by Dr. Burger and myself (Das Entstehen des He Spektrums bei elektrischer Anregung, *Ztsch. f. Phys.*, 51, 34, 1928) and partly by Mr. Elenbaas. The details of the latter's work will be published soon.

UTRECHT,
TUXEDO,
March 29, 1929.

ELECTRON WAVES.

BY

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Bell Telephone Laboratories, Inc.

IT is now two years, lacking one day, since the first results were published on the diffraction of electrons by crystals. Since that time there have been reports of some twenty-five or thirty investigations which add to the evidence that in their interactions with crystals, electrons behave as if they were waves; also a dozen or more notes and papers have appeared in which the theoretical aspects of this phenomenon have been considered. Conspicuous among these are a valuable paper by Dr. Hans Bethe, a student of Prof. Sommerfeld's, on the general subject of electron diffraction, and an important article by Prof. C. G. Darwin on the possibility—or, perhaps I should say the impossibility—of polarizing electron waves by reflection.

The present occasion is an appropriate one for reviewing briefly the experimental work which has been done during these two years in this new field of research, and for indicating paths along which future experimentation may be expected to proceed.

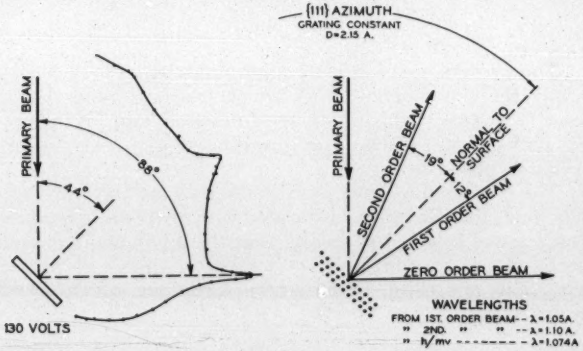
The outstanding results so far obtained are three in number—first, that the waves associated with electrons of momentum p are of length h/p; second, that the interaction between electrons and a metal involves something similar to optical refraction; and third, that electron waves are not polarized by reflection.

The lengths of electron waves have been determined in six or eight different investigations, in all of which the de Broglie formula, just stated, has been verified within the limits of accuracy of the measurements. Observations have been made upon diffraction patterns formed in some of these experiments by single crystals, in some by thin films of polycrystalline metals, and in two at least by ordinary ruled

gratings. The electrons used in the various tests have had speeds corresponding to accelerating potentials ranging from 10 to 80,000 volts—or to wave-lengths ranging from 4 to 0.05 A. In the more accurate experiments the wave-lengths computed from the diffraction data differ from those calculated from the de Broglie formula by less than one part in one hundred. So far as wave-length measurements are concerned we may look forward, I think, only to a more precise verification of the theoretical relationship.

The evidence that electron waves are refracted is contained in experiments made by Dr. Germer and myself, and in certain experiments by Rupp. It consists in this, that certain differences are observed between the diffraction patterns formed by low speed electrons and those formed by x-rays, and that these differences are of a type which might result from ordinary optical refraction of the waves by the crystal.

FIG. 1.



The nature of the evidence is well illustrated by some rather interesting, but as yet unpublished results which were obtained in our laboratory some months ago. Electrons which had been accelerated through 130 volts were directed at 44 degrees incidence against the face of a nickel crystal as indicated on the left in Fig. 1. The distribution of elec-

trons scattered in the plane of incidence is shown by the curve, and it will be noted that there is preferential scattering in three different directions. The preference may seem not so very marked, but this is because the curve shows the distribution of electrons of all speeds instead of those of the highest speed only. The preferred directions are shown again in the figure on the right. The beam, for which the deflection is least, stands exactly in the direction of regular reflection, and is the analogue of the Bragg x-ray beam. The speed of the incident electrons was adjusted to bring the intensity of this beam to a maximum, and it is merely a coincidence that these others, which are the analogues of certain Laue beams, are at or near intensity maxima under the same conditions.

The regularly reflected beam lies, of course, in the direction of a beam which would be observed with x-rays; these others, however, do not. They do not lie accurately in directions of regular reflection from sets of densely packed atom planes of the crystal as they would if the observations were for x-rays. Now departures from this simple condition would be expected to occur, if owing to refraction there were changes in the direction and wave-length of the electron beam where it enters and leaves the crystal. The Bragg law might obtain inside the crystal, but the beams outside would not be the prolongations of those within, and the Bragg formula could not be used to calculate wave-lengths from the angle between them. Exactly the same thing would happen with x-rays if the index of refraction of the crystal were sufficiently different from unity.

It may be shown that if the beam displacements which we here observe are in fact due to refraction wave-lengths can be calculated, nevertheless, and without knowledge of the refractive index of the crystal, by merely referring the beams to the atomic plane grating formed by lines of atoms lying in the surface of the crystal and extending at right angles to the plane of incidence.

When this procedure is adopted we find that the beams shown in Fig. 1 are correctly placed to be zero, first and second order diffraction beams of the surface grating. The constant of the grating is 2.15 A. For the first order beam we obtain a wave-length 1.05 A, for the second order 1.10 A,

and the de Broglie wave-length for 130 volt electrons lies just midway between these values.

It may seem from results such as these that electron waves are indeed refracted in just the same way as light and x-rays. Such a conclusion would, however, be premature, for there are various laws of refraction other than those of ordinary optics which leave the plane grating law valid. It has yet to be determined whether the refractive index which we assign to the crystal to explain the distortions of the patterns is, as in optics, a function of wave-length only.

The only other experiments in which evidence of refraction has been found are some by Rupp on the diffraction of rather low speed electrons by thin films of polycrystalline metals. The diameters of the diffraction rings observed in these experiments differ slightly from those computed from the constants of the crystals and the de Broglie wave-lengths. Rupp ascribes these differences to refraction and uses their values to compute refractive indices of the metals.

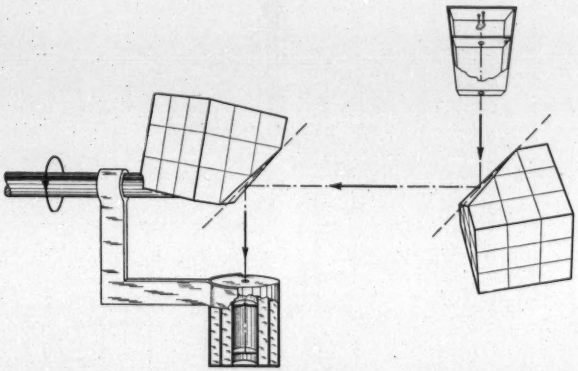
The interpretation which Rupp gives to his observations has, however, been questioned by G. P. Thomson who shows that refraction may be expected to produce a much smaller effect in experiments of the type made by Rupp and by himself than Rupp supposes. But now it is mentioned in a recent note by Rosenfeld that Rupp is not impressed by Thomson's criticism, so that the study of electron waves has already progressed so far as to acquire a mild controversy.

The problem of the refraction of electron waves by metals requires much more study than it has so far received. It is of importance not only in itself, but because of the bearing which it has on the new Fermi-Sommerfeld theory of electrons in metals.

Another problem which must be taken up seriously is that of the relative intensities of the various beams constituting the electron diffraction pattern. The study of intensities in x-ray diffraction patterns enables us to infer the distribution of electron charge within the unit cell of the crystal. The like analysis of the electron patterns should enable us to infer the distribution of electrostatic potential. A theoretical basis for the interpretation of results of this kind has been set up by Bethe in the paper to which I have already referred.

A number of physicists in different parts of the world have made tests to determine if electron waves are polarized by reflection. Four experiments of this kind have been reported during the last several months, and in three of the four the results have been definitely negative. The exception is an experiment with β-rays performed by Cox, McIlwraith and Kurrelmeyer in which they find some evidence of asymmetry produced in an electron beam by reflection, but of a type

FIG. 2.

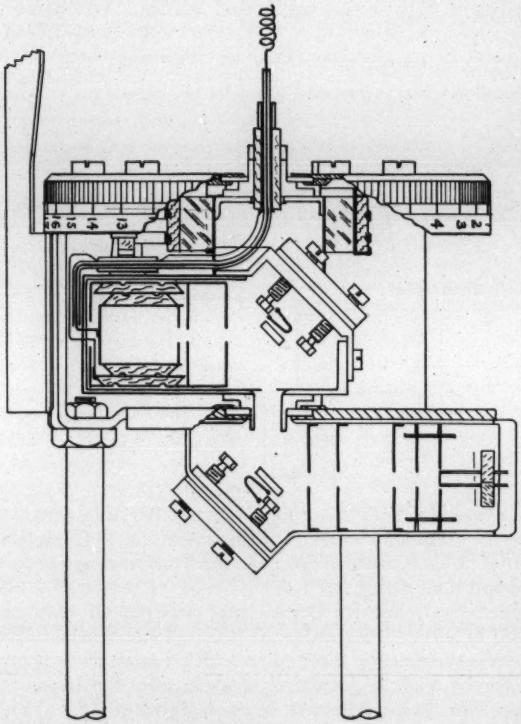


unlike that met with in optics. Cox and his collaborators are, however, none too confident of this result, and I think that we shall be obliged, until more data are forthcoming, to reserve judgment concerning it.

The tests made by Dr. Germer and myself may be described in a very few words. A beam of electrons is reflected successively from the faces of two nickel crystals as shown in Fig. 2—the angle of incidence of each reflection being 45 degrees. The twice reflected beam is received in a Faraday box collector, and its intensity is measured as the second reflector and the collector are rotated about the beam proceeding from the first crystal to the second. The experiment is similar to that performed with the Norrenberg mirrors by which one demonstrates the polarization of light by reflection

from glass. If electron waves are polarized by reflection we should expect the current entering the collector to be a maximum when the planes of incidence of the two reflections

FIG. 3.

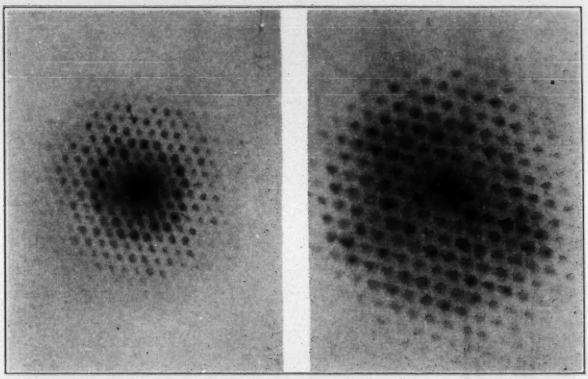


are parallel, and a minimum when they are at right angles. A diagram of the actual apparatus is shown in Fig. 3. The observation is that within the limits of uncertainty of our measurements—about one-half of one per cent.—the current

of electrons which survive the two reflections without loss of energy is independent of the azimuth of the second reflector. This result is in accord with a prediction made by C. G. Darwin who has used Dirac's equations of the electron in considering the question of polarization.

Similar tests have been made by Joffe and Arsenieva with polycrystalline targets of various materials; and Wolf has tested for polarization by reflection in a magnetic field. In both cases the results were negative.

FIG. 4.

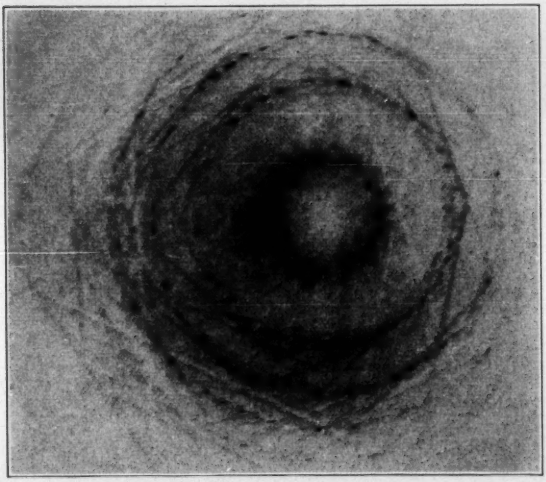


Of all of the experiments which have been reported the most beautiful are, I think, the recent ones of Kikuchi on the diffractions of high speed electrons by mica. These experiments are described in *The Japanese Journal of Physics*, and are, I imagine, unknown to many in this audience. I have, therefore, had plates prepared of some of Kikuchi's patterns which I am sure you will be interested in seeing.

The patterns shown in Fig. 4 are for electrons of two different speeds diffracted by an extremely thin sheet of mica. The molecules in the cleavage face of mica form a triangular array, and the remarkable thing about these patterns is that they are just the ones which would be formed if the diffracting system were a single layer of molecules only. The speci-

men is, however, fifty or more layers in thickness, and we naturally ask how a crystal comprising so many layers can produce the pattern of a two dimensional grating. A possible explanation is to be found, I think, in a lack of coherence among the waves proceeding from the different layers. The lengths of the waves used in these tests are only about 1/200 of the distance between successive layers of molecules so that

FIG. 5.



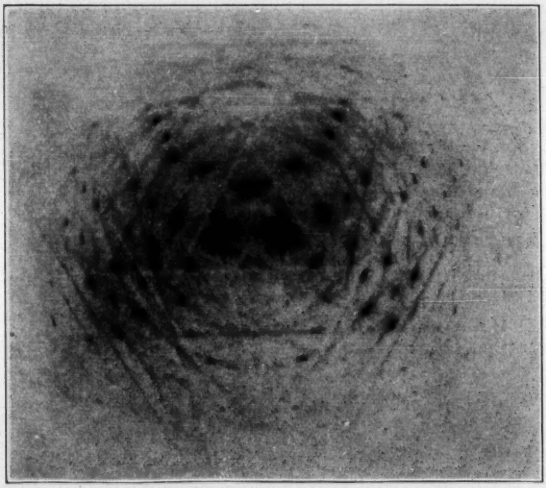
only very slight departures from the normal spacing are sufficient to produce complete incoherence and the observed pattern. Such departures are easily imagined in a crystal which cleaves as readily as mica, and in a thin specimen which has been subjected undoubtedly to considerable manipulation.

The pattern shown in Fig. 5 is for a thicker crystal, and that in Fig. 6 for one which is thicker still. As the thickness of the crystal is increased there is a gradual development of the features characteristic of diffraction by three dimensional

gratings. These experiments by Kikuchi and Nishikawa open up a most attractive field of investigation.

To the various problems calling for investigation which I have already mentioned, I would like to add yet another, and one of very great importance. The elements of any wave motion are, as we know, the three interrelated quantities, wave-length, frequency, and phase velocity. Observa-

FIG. 6.



tions on diffraction phenomena enable us to calculate wave-lengths, but since the data do not include measurements of time they can tell us nothing of the frequencies of the waves or of their velocities. What we require for electron waves is a measurement of one or the other of these quantities, but how such measurements are to be made is not all clear. The difficulties which one anticipates seem quite insuperable.

The phase velocities are all of them greater presumably than the velocity of light, and the frequencies are none of

them less than m_0c^2/h or about 10^{20} per second. We may expect that if a homogeneous beam of electrons is cut or intercepted at regular intervals, the electrons in the beam beyond the point of cutting will no longer be homogeneous, but will have speeds over a range extending above and below the original value. The magnitude of this effect will depend upon the ratio of the frequency of cutting to the frequency of the waves. If it could be made large enough for detection and measurement the frequencies of electron waves could be calculated. But at present this experiment seems outside the realm of practicability by a discouraging number of orders of magnitude.

BELL TELEPHONE LABORATORIES,
NEW YORK, N. Y.,
April 15, 1920.

A NEW WAVE-LENGTH STANDARD FOR X-RAYS.

BY

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University of Chicago.

THE first reliable value of the wave-length of an X-ray beam was obtained when Bragg[1] determined the atomic arrangement in a rock salt crystal, and used the calculated distance between its layers of atoms as a standard for measuring the wave-length of the palladium K line. The wave-length is given by the Bragg formula,

$$n\lambda = 2D \sin \theta, \tag{1}$$

where n is the order of the spectrum, D is the distance between successive layers of atoms, and θ is the glancing angle of diffraction. When one takes into account the refraction of the X-rays as they enter the crystal, this relation becomes,

$$n\lambda = 2D \sin \theta \left(1 - \frac{1 - \mu}{\sin^2 \theta} \right), \tag{2}$$

where μ is the index of refraction. In this equation n is a known integer, θ can be measured with high precision, and $1 - \mu$ can be measured accurately enough so that its uncertainty introduces no appreciable error in the result. The wave-length λ can thus be measured as accurately as D is known.

The grating constant of a crystal whose structure is known can be calculated in terms of Avogadro's number. Thus for a simple cubic crystal,

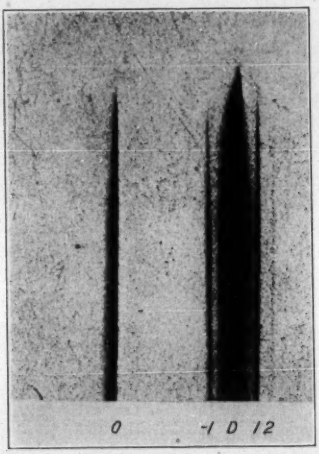
$$D = (W/N\rho)^{1/3}, \tag{3}$$

where W is the molecular weight, N is the number of atoms per gram atom, and ρ is the crystal density. For other than simple cubic crystals, the right hand side of equation (3) must

[1] W. L. Bragg, *Proc. Roy. Soc. A.*, 89, 248 (1913).

be multiplied by a simple numerical factor. In this equation, the molecular weight is thought to be known with high precision. The density can be precisely measured, though there may be some question whether the measured density of a large crystal is identical with the density of the perfect crystal lattice which is postulated in deriving this equation. The chief uncertainty in the grating space would seem to be that

FIG. 1.



Spectrum of Mo K_{α_1} line from grating ruled on speculum metal, 50 lines per mm. (Doan and Compton, 1925) D = direct beam, 0 = zero order (direct reflection).

due to the uncertainty in Avogadro's number. This is estimated by Millikan to be known to about 1 part in 1,000, which means an uncertainty in D and hence also in λ of about 1 part in 3,000.

About four years ago Dr. Doan and I found that it is possible to secure X-ray spectra from ruled reflection gratings if the X-rays are allowed to strike the reflecting surface at a sufficiently sharp glancing angle. One of our spectra, of the $K\alpha$ line of molybdenum, is shown in Fig. 1. From such a spectrum it is possible to measure the wave-length in terms

of the spacing of the lines ruled on the grating, which can in turn be measured directly. Though the angle of diffraction is much smaller than that occurring when the crystal grating is used, it seemed from the start that the definiteness of the grating space of the ruled grating should make it preferable for making absolute determinations of X-ray wave-lengths.

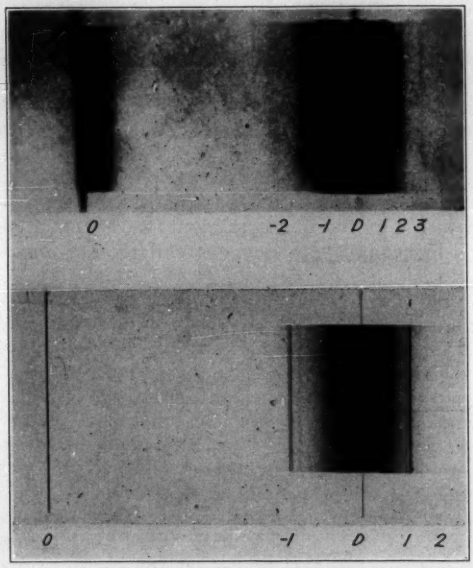
In these first ruled grating measurements, our probable error was about 0.4 per cent., and to this accuracy we found our results in accord with the crystal values. Since that time similar spectra have been obtained using more refined methods by such investigators as Thibaud,[2] Hunt,[3] Bäcklin,[4] Wadlund[5] and others. There has been a definite tendency for the wave-lengths as measured by these men to be greater than those measured on the same spectral lines by the crystal method, though in most cases the difference has hardly been larger than the probable experimental error. During the last year, however, Dr. J. A. Bearden, working at Chicago, has made measurements by the ruled grating method[6] that seem to be of much higher precision than those of the previous investigators. In Fig. 2 are shown spectra obtained by Wadlund (above) and Bearden (below), both using a grating of the same characteristics as that from which Fig. 1 was made. A comparison of these three spectra shows the gradual improvement of technique. Bearden's measurements result in a wave-length 0.24 per cent. greater than that given by Siegbahn from crystal measurements. This difference is about 25 times the probable error of his measurements, and thus seems to indicate a hidden error in our wave-length estimates based on crystal diffraction.

If one calculates from the X-ray wave-lengths as thus determined the crystalline grating space, and thence Avogadro's number and the charge on the electron, one finds values for these constants which differ by a surprisingly large amount from the accepted values. It will therefore be worth while to discuss some of the X-ray wave-length measurements using ruled gratings, and to look for possible errors which may be present.

[2] J. Thibaud, *Comptes Rendus*, 182, 55 (1926), *Rev. d'Opt.*, 5, 97 (1926).
[3] F. L. Hunt, *Phys. Rev.*, 30, 227 (1927).
[4] E. Backlin, Thesis, Upsala (1928).
[5] A. P. R. Wadlund, *Phys. Rev.*, 32, 841 (1928).
[6] J. A. Bearden, *Proc. Nat. Acad. Sci.*, June (1929).

In making such standard wave-length measurements, one must choose between the use of soft X-rays of comparatively great wave-length, for which the angles to be measured are relatively large, but for which a vacuum spectrometer is necessary, and the use of ordinary X-rays, for which the angles to be measured are inconveniently small, but for which the

FIG. 2.



Upper figure, Wadlund's spectrum of NCuKα from 50 line grating; lower figure, Bearden's spectrum of CuKα and Kβ lines from the same grating.

necessary adjustments can be made and continually checked in the open air. Bäcklin's experiments were done using a vacuum spectrometer and relatively long wave-lengths. Bearden and Wadlund chose the latter alternative, having in mind also that for the ordinary X-rays the index of refraction is more accurately known, and the comparison with the crystal wave-lengths is of correspondingly greater significance.

The angles to be measured, using the latter method, are less than 40 minutes of arc. Such angles may be measured by the help of a finely divided circle, by the use of a telescope and scale, or by measuring the separation of the X-ray lines on a photographic plate placed at a known distance. Wadlund, following a suggestion made by Doan, relied upon the telescope and scale. In any case, however, the separation of the lines on a photographic plate must be used in some part of the experiment, and Bearden preferred to measure all of his angles by this means.

It will not be necessary here to describe Bearden's experiment in detail, since this has been done elsewhere.[7] One should perhaps mention, however, that by taking photographs on two plates at a known distance apart, he determines the wave-length from the formula,

$$n\lambda = \frac{D}{2b^2} \frac{(y - x)^2(y \pm z)z}{y^2} . \qquad (4)$$

Here n is the order of the spectrum, D is the grating space, b is the distance between the two plates, and x, y and z are distances between lines on the plates themselves. Thus every quantity that needs to be known is susceptible to precise direct measurement.

It will be interesting to compare the results of different investigators who have used the ruled grating method:

TABLE I.

Investigator.	Spectra Line.	λ	Grating λ − Crystal λ.	Probable Error.	Date.
Compton-Doan...	MoKα_1	.7078A	− .1%	± .4%	1925
Thibaud.....	CuKα	1.540	+ .1	± 1.	1926
Hunt.....	PtMα	6.1	+ 1.6		1927
	AlKα	8.5	+ 2.0		
Bäcklin.....	MoLα	5.402	+ .1	± .2	1928
	AlKα	8.333	+ .2	± .1	
	MgKα	9.883	+ .2	± .2	
	FeLα	17.61	+ .1	± .2	
Wadlund.....	MoKα_1	.708	+ .1	± .1	1928
	CuKα_1	1.537	0	± .08	
	FeKα_1	1.938	+ .3	± .2	
Howe.....	ZnLα	12.24	+ .2	± .3	1929
	CuLα	13.31	+ .6	± .3	
	FeLα	17.61	+ .5	± .3	
Bearden.....	CuKα	1.5422	+ .23	± .01	1929
	CuKβ	1.3926	+ .24	± .01	

[7] J. A. Bearden, *Proc. Nat. Acad.*, June 1929.

It will be noted that there is a consistent tendency for the ruled grating wave-lengths to have higher values than the wave-lengths measured from crystals. Though in most cases the difference is hardly greater than the probable error of the measurements, Bearden's experiments, which appear to be much the most precise, show an outstanding discrepancy from the crystal values.

The only case in which there is an apparent conflict between Bearden's experiments and the results of other grating measurements is Wadlund's value for the $K\alpha_1$ line of copper. To see whether this difference is significant, let us note the individual values from which Wadlund's mean result is taken. He found:

TABLE II.

Plate No.	Order.	Wave-length.	Grating λ − Crystal λ
105	1	1.5394 ± .0016	+.14%
	2	1.5361 ± .0011	−.08
	3	1.5378 ± .0008	+.03
106	1	1.5312 ± .0028	−.40
	2	1.5330 ± .0008	−.28
	3	1.5427 ± .0011	+.34
	4	1.5423 ± .0009	+.32
	6	1.5359 ± .0005	−.09

It will be seen that orders 3 and 4 from his plate 106, which would seem to be two of his best measurements, give wave-lengths larger than Bearden's mean result. (Bearden used the unresolved $\alpha_1\alpha_2$ doublet, whereas Wadlund used only the α_1 component). In order to be certain that the difference was not a real one, Bearden repeated the measurement on the copper $K\alpha$ line using Wadlund's own grating, and with the advantage of the knowledge of the possible sources of error in Wadlund's experiments. The result was entirely consistent with Bearden's measurements using his other gratings.

It is perhaps worth noting that the sharpness of the best lines on Bearden's plates is such that an error in setting great enough to make his results agree with the crystal measurement would mean placing the cross hair of the comparator microscope beside the line instead of over it.

CONSEQUENCES OF THIS ABSOLUTE WAVE-LENGTH MEASUREMENT.

Using the value of the wave-length of the copper Kβ line as found by Bearden, the grating space D of a calcite crystal can be obtained from equation (2). Siegbahn and Dolejsek[8] find for θ in this case 12° 15′ 28.2″ for $n = 1$, with the calcite crystal at 18° C.; whence $\sin\theta = 0.229334$. The writer has given[9] for the value of $(1 - \mu)/\sin^2\theta$ for calcite, 1.46×10^{-4}. These data give for the grating space of the calcite (100) planes,

$$D_{\text{calcite}} = 3.0366 \pm .0004\ A.\ (18°\ \text{C.}),$$

and

$$D_{\text{calcite}} = 3.0367 \pm .0004\ A.\ (20°\ \text{C.}). \qquad (5)$$

From a relation similar to equation (3) we find for Avogadro's number,

$$N = \frac{nM}{\rho\varphi}\frac{1}{D^3}, \qquad (6)$$

where for calcite,

$$n = \tfrac{1}{2},$$
$$\rho = 2.7102 \pm .0004 \text{ g. cm.}^{-3},^{10}$$
$$M = 100.078 \pm .006,^{11}$$
$$\phi = 1.09630 \pm .00007,^{12}$$
$$D = 3.0367 \pm .0004 \times 10^{-8} \text{ cm. (Eq. 5).}$$

Thus,

$$N = 6.0142 \pm .0026 \times 10^{23}\text{mole}^{-1}. \qquad (7)$$

Knowing Avogadro's number, the electronic charge e is given in terms of Faraday's constant of electrolysis F by the relation,

$$e = F/N. \qquad (8)$$

Using the value[2] $F = 9648.9 \pm .7$ e.m.u., and $c = 2.99796 \times 10^{10}$ cm./sec., we thus obtain

$$e = 4.810 \pm .002 \times 10^{-10}\text{e.s.u.} \qquad (9)$$

[8] M. Siegbahn and V. Dolejesek, *Zs. f. Phys.*, 10, 160 (1922).
[9] A. H. Compton, "X-rays and Electrons" (1926), p. 212.
[10] O. K. DeFoe and A. H. Compton, *Phys. Rev.*, 25, 618 (1925).
[11] R. T. Birge, *Phys. Rev.*, Sup. 1 (1929).
[12] H. N. Beets, *Phys. Rev.*, 25, 621 (1925).

Perhaps the most direct method of obtaining a value of Planck's constant h on the basis of this work is through the measurement of the limit of the X-ray spectrum by Duane and his collaborators. Writing the Duane-Hunt law in the form

$$h = Ve\lambda/c,$$

where V is the potential applied to the X-ray tube, and λ is the minimum wave-length, and expressing λ by equation (2), remembering that for this experiment $n = 1$, we get

$$h = \frac{2}{c} VeD \sin\theta(1 - b), \tag{10}$$

where $b = (1 - \mu)/\sin^2\theta = 1.46 \times 10^{-4}$. The experiments of Duane, Palmer and Chi-Sun-Yeh[13] give directly the value of $V \sin\theta$ as 2039.9 ± 9 volts. Using the values of e and D obtained above, we thus obtain

$$h = 6.629 \pm .004 \times 10^{-22} \text{ erg sec.} \tag{11}$$

If we write Bohr's expression for the Rydberg constant in the form,

$$R = 2\pi^2 \frac{e^5 m}{h^3 e}, \tag{12}$$

we may solve for the value of e/m. Using[14] $R = 3.28988 \times 10^{15}$ we thus find

$$e/m = 1.769 \pm .003 \times 10^7 \text{ e.m.u./g.} \tag{13}$$

A comparison of the values thus obtained with the accepted values found by other methods, as recently summarized by Birge,[14] is given in the following table.

TABLE III.

Comparison of Values of Fundamental Constants.

	From Bearden's Wave-lengths.	Accepted Values.	Per cent. Difference.
D Calcite	3.0367 A.	3.0283 A.	0.3
N	6.014×10^{23}	6.064×10^{23}	0.8
e	4.810×10^{-10}	4.770×10^{-10}	0.8
h	6.629×10^{-27}	6.547×10^{-27}	1.2
e/m	1.769×10^7	1.769 (deflection)	0
		1.761 (spectrum)	0.5

[13] W. Duane, H. H. Palmer, and Chi-Sun-Yeh, *J. Opt. Soc. Am.*, 5, 376 (1921).
[14] R. T. Birge, *Phys. Rev.* Sup. 1, (1929).

The probable error of every value in the table as estimated by the usual methods is less than 0.1 per cent. The large differences thus point strongly toward a hidden error either in the experiments or in the formulæ relating the experimental data to these fundamental constants. The most significant differences are those in the values of e and of e/m, since these quantities are subject to independent experimental measurement. The accepted values of N, D and h are all based upon the experimental value of e, so the differences in their values give but little additional information. We have been diligently searching for such a hidden error for the past six months without success, and it now seems necessary to appeal for help by calling the discrepancies to your attention.

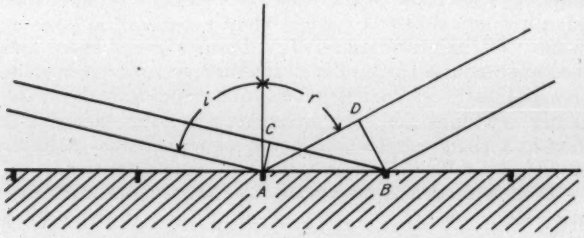
It is interesting however to note that if one uses these new values of e and h, better agreement is found with Eddington's recent speculations [15] regarding Sommerfeld's α. He has brought forward reasons for believing that $1/\alpha$ should be the integer 136, where $\alpha = 2\pi e^2/hc$. Using the accepted values of e, h and c, we find $1/\alpha = 137.2$, which seems to differ by more than the experimental error. The values given above, however, lead to $1/\alpha = 136.45 \pm .15$ which is not far from Eddington's value. While one cannot say that the theoretical argument leading to this value is cogent, it is suggestive that the one integer which can have significance is in close agreement with these new values of the constants.

Possible Sources of Error.—We have been unable to locate any errors in the technique of the experiments which could introduce an error in the wave-length as large as 0.3 per cent. The use of the wide variety of gratings was suggested by the thought that there might be some error in the grating formula (4). The fact that different gratings gave the same results, and that measurements of different orders of spectra led to the same wave-lengths, confirmed the validity of the formula. One may perhaps however call attention to a very general proof of this equation which indicates that no surface peculiarity of the grating can in any way affect the angle of diffraction. In Fig. 3 is shown diagrammatically the simple case of diffraction of two rays from adjacent lines of the reflection grating.

[15] A. S. Eddington, *Proc. Roy. Soc.*, A, 122, 358 (1929).

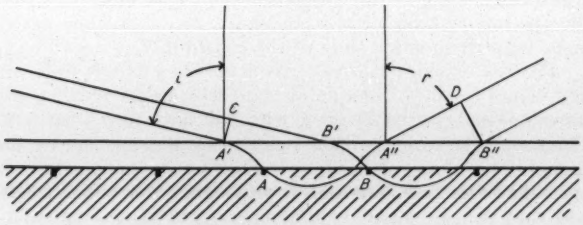
The condition for an interference maximum at the angle r is that $\overline{CB} - \overline{AD} = n\lambda$, where n is an integer. In Fig. 4 we have supposed that due to refraction or some other cause the ray diffracted from the slit A traverses and irregular path

FIG. 3.



$A'AA''$ while in the neighborhood of the grating, but that when beyond some arbitrary plane $A'B'A''B''$ it is propagated in a straight line. If the ray diffracted from the adjacent slit B traverses a path of the same shape, and through media of the same refractive index, the phase lag along $B'BB''$ will be the

FIG. 4.

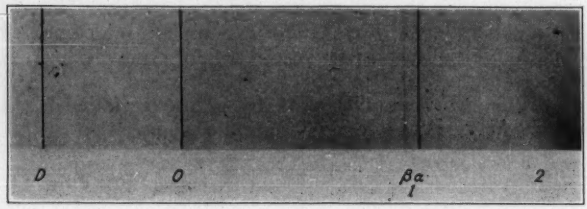


same as that along $A'AA''$. Thus here again the interference maximum occurs when $\overline{CB'} - \overline{A''D} = n\lambda$. Since $A'B' = AB = A''B''$, this means that the angles i and r are the same as those of the simple case in Fig. 3, from which equation (4) follows.

I can accordingly find no basis on which to doubt the reliability of the wave-length values resulting from Bearden's experiments.

The passage from the wave-length to the crystal grating space through equation (2) seems so direct as to admit little chance of error. A question might occur regarding the effect of refraction. The correction for refraction introduced in this equation has been verified by thorough theoretical studies by Darwin[16] and Ewald,[17] Moreover, the fact that the equa-

FIG. 5.



Bearden's spectrum of CuK series from glass grating of 600 lines per mm.

tion as thus corrected leads to the same wave-length for the different orders of reflection is a strong experimental confirmation. This fact also makes untenable the suggestion that the spacing of the crystal lattice may change near the surface of the crystal.

Avogadro's number it would seem involves no additional uncertainty except that of the crystal density. The existence of crystal faults is well known, and Joffe[18] and Zwicky[19] among others have emphasized the existence of resulting gaps in the crystal lattice. It should follow that the minute crystal elements would have a higher density than the large scale crystals. Unfortunately such a difference is in the wrong direction to account for the difference between the crystal and the ruled grating wave-lengths. A large impurity of high molecular weight might account for the difference; but it is improbable that such an impurity exists. It should be noted also that the difference is nearly the same whether a

[16] C. G. Darwin, *Phil. Mag.*, 27, 318 (1914).
[17] P. Ewald, *Phys. Zeits.*, 21, 617 (1920).
[18] A. Joffe, "The Physics of Crystals" (1928).
[19] F. Zwicky, *Proc. Nat. Acad.*, 15, 253 (1929).

comparatively perfect crystal such as calcite is used or whether one employs the relatively imperfect crystal, rock salt.

From Avogadro's number the relation through Faraday's constant of electrolysis to the electronic charge seems straightforward.

Such directly conflicting experimental evidence regarding these fundamental constants is not a new problem. Thus for example there is the outstanding difference in the values of e/m as determined by deflection experiments as compared with that resulting from spectroscopic observations. It would seem that the best mode of attack would be the redetermination of these constants by whatever independent methods may be capable of giving sufficient precision.

IMPROVED TECHNIQUE FOR THE EXCITATION OF THE RAMAN EFFECT WITH A SPECIAL REFERENCE TO GASES.

BY

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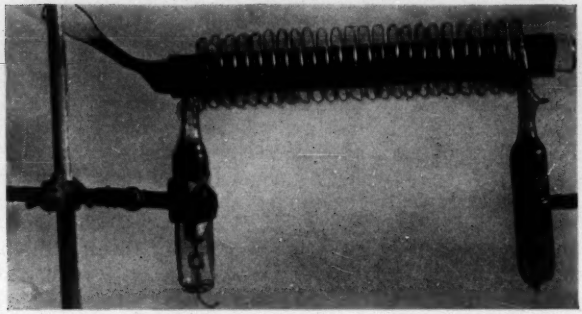
Johns Hopkins University.

UP to the present time the mercury arc has been used exclusively as a source of radiation for the excitation of the Raman effect. Even when separated by suitable filters the mercury radiations are not well adapted to the work, as it is impossible to obtain a pure mono-chromatic excitation which is necessary for obtaining a unique Raman spectra. If we excite, for example, by the group of three lines at wave-length 4358 we obtain Raman lines excited by all three members of the group, and it is impossible to identify them until the wave-lengths and frequencies for all have been computed, and the frequencies subtracted from those of the three exciting lines. The same trouble occurs with 4046 and its companion 4077. If we excite by both groups of lines without using filters, the spectrum excited by 4046 is in part superposed on that excited by 4358, which adds to the confusion. I have, accordingly, made a very careful search for a source of mono-chromatic radiations of sufficient intensity to excite the Raman spectrum of fluids, and have finally adopted the helium discharge, employing the strong line of wave-length 3888.6. If the light of the helium tube is filtered through glass stained with nickel oxide, the helium line in question is more than one hundred times as strong as any other transmitted line, and the Raman spectrum is made up of lines excited by the single wave-length only. The apparatus is shown in Fig. 1. It consists of a tube about 10 feet in length, wound into a tight spiral about 2½ inches in diameter. This tube is furnished with copper electrodes, and was made by the Claude-Neon Lamp Company of Baltimore. It is operated by a transformer giving a potential of 20,000 volts,

with a current strength of about 25 milliamperes. Within this tube is a second tube open at both ends, and made of nickel oxide glass, transparent only to ultra-violet light. Within this tube is a third tube of transparent glass, one end of which is flattened, ground plane, and polished, the other end drawn off to an oblique funnel, painted black on the outside to provide a black back-ground against which the

FIG. 1.

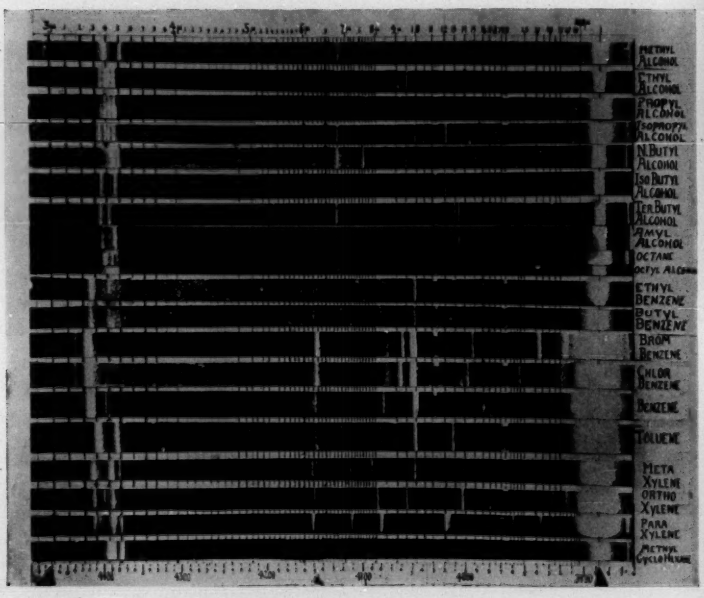


excited liquid is viewed by the spectroscope. The tube of nickel oxide glass is supported on two small pads of asbestoes which prevent it from coming in contact with the helium spiral. An electric fan delivers a strong blast of air against the tube to prevent overheating. With this arrangement the Raman spectra can be photographed with exposures of from 8 to 16 hours. This is much longer than the time necessary with the mercury arc, but this disadvantage is amply compensated by the fact that a single Raman spectrum lies spread out before us, uncontaminated by anything save two faint helium lines which cannot be wholly suppressed by the filter. With spectra of this nature it is no longer necessary to measure the wave-lengths and calculate the frequencies, for the spectrograms can be enlarged to a suitable scale and pasted on a card in coincidence with suitable lines of a scale of wave-length previously ruled on the card. I have prepared such a scale of wave-lengths, representing the values in μ of

the infra-red absorption bands, for the various Raman lines based on the supposition that the infra-red frequencies correspond to the differences of the Raman line frequencies subtracted from that of the helium line 3888. The scale of wave-lengths was prepared by first computing wave-lengths the frequencies corresponding to which when subtracted from the frequency of 3888 would give frequencies corresponding to 3 μ, 3.1 μ, 3.2 μ and so on, up to 100 μ. The computations for tenths were made only for the low values of μ. A photograph of the iron spectrum was made with the same spectrograph employed in making the Raman photograph. This spectrum was then enlarged about twenty-fold, and a wave-length scale prepared to fit it. This scale was pasted at the bottom of a large sheet of cardboard and the points marked on it corresponding to the calculated wave-lengths above mentioned. Vertical lines were then drawn from these points to the top of the sheet of cardboard. These lines represented the μ values of the Raman lines on photographs enlarged to the same scale and attached to the cardboard in proper register. The registration was effected by the two faint helium lines which I have already referred to (3964 and 4026), which lie near the exciting line, and a third helium line 4471, just beyond the long wave-length limit of the Raman spectra, which appeared on most of the plates as a result of reflection from the walls of the room to the slit of the spectrograph. Photographs of the Raman spectra of nine of the alcohols and ten benzene substitution products are reproduced on plate 1. We see that all of these spectra are characterized by a strong group of lines associated with infra-red absorption in the vicinity of 3.4 μ, but that the number of lines in the group and the position of the center of gravity of the group shift as we pass from one spectrum to another. It will be noticed that in this group we have for ethyl-benzene and butyl-benzene the line corresponding to benzene and also the group which appears in the case of ethyl- and butyl-alcohol. Between this point and the 6 μ, no Raman lines at all appear in any of the compounds, but between the 6 μ and 90 μ we have a large number of lines, some of them common to the different members of the series, and others occupying different positions as we pass from one

substance to another. All that I have said thus far is based on the interpretation of the Raman lines which was given at first, but, as has been pointed out by Langer, it now seems certain that the lines in the vicinity of the exciting lines are not associated with absorption bands of very long wave-length

PLATE I.



in the infra-red, but correspond to transitions between levels which represent absorption bands in the region already explored by infra-red spectrometers. That this was true numerically was shown by Langer in the case of carbon tetrachloride. The group of three strong lines which appeared on both sides of the exciting line, and which were previously associated with infra-red bands of wave-length 22 μ, 32 μ and 46 μ were in reality connected with transitions between

levels corresponding to absorption bands found in the region between 3 μ and 12 μ. The μ values on the chart reproduced which was prepared before the publication of Langer's note in Nature have no significance according to our present view. In future work charts should be prepared on which the frequencies of the Raman lines can be read off directly. In the present case these frequencies can be determined from the wave-lengths given at the bottom of the chart.

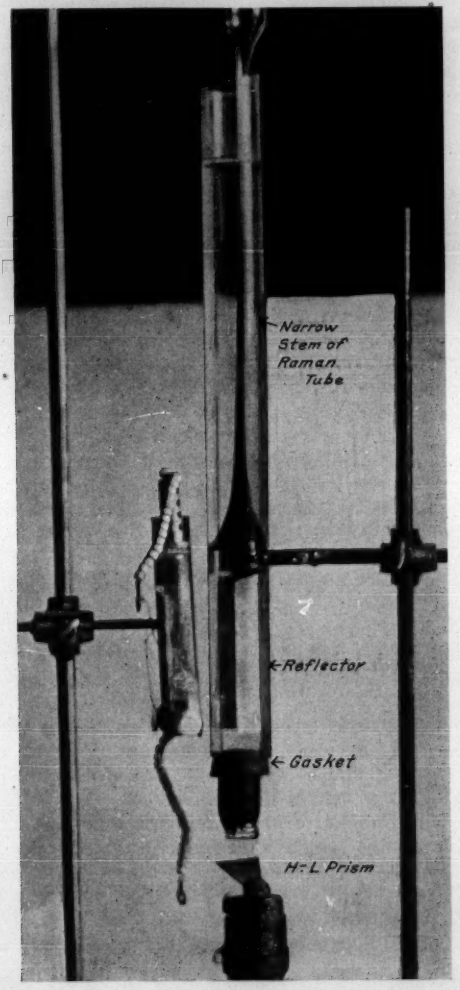
For the benefit of those who are obliged to use the mercury arc for the excitation of the spectra, and it may be some little time before tubing of nickel oxide glass is on the market, I may mention briefly an improved method of cooling the tube which avoids the necessity of employing running water.

A photograph of the system is shown in Fig. 2. A vertical tube of glass about 2 inches in diameter (internal), and 2 feet long is mounted vertically in a clamp stand. The Raman tube is mounted within this passing through a gasket made from a large rubber stopper. The space between is filled with water or with a solution containing a suitable coloring matter, if absorption of one of the mercury lines is desired. The Raman tube is drawn down as shown in the photograph, the upper end being left open to provide for expansion of the fluid. A reflector of thin sheet aluminum partially surrounds the inner tube, and the vertical quartz mercury arc is mounted as close as possible to the outer tube opposite to the reflector. The lower end of the Raman tube is either blown flat ground and polished, or blown out in a very thin bulb, subsequently flattened in the flame. Directions for making such a tube will be found in a paper appearing in the *Philosophical Magazine* for May.

The cooling is effected by circulation of the water by convection currents, the temperature not rising above 60°. If very volatile liquids are to be studied the arc can be moved away to a suitable distance.

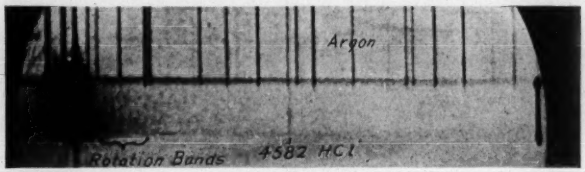
I should now like to draw your attention to some very interesting results which have been obtained with hydrochloric acid gas and ammonia at atmospheric pressure, excited by the light of the mercury arc. A very special technique is required for the excitation on account of the weakness of the light, nevertheless records have been secured

FIG. 2.



with exposures of only five hours with an F2 one-prism spectrograph by employing apparatus which I shall describe presently. In the case of hydrochloric acid it was found that a single strong line of $\lambda = 4581.8$ appeared the frequency of which when subtracted from that of the exciting line 4046 gave the frequency of the missing line of the infra-red absorption band at 3.4645 μ. The Raman line in this case does not

FIG. 3.



identify itself with an absorption line but corresponds to the head of the Q branch (vibration with rotation change) not observed in absorption. Professor Kemble has calculated that the missing line should have a wave-length of 3.4649 μ and the Q branch 3.4689 μ. My value of 3.466 is in very fair agreement with this calculation. There are also a number of nearly equi-distant lines close to the 4358 mercury line, which I first thought might be interference maxima due to the passage of the light of the faint continuous spectrum through the very thin wall of the glass bulb, but I now feel sure that they are real, as I have obtained them always in the same position with bulbs of different thicknesses. If we assume these to be excited by the light of the 4358 line they may be identified with the rotation bands found by Czerny (*Zeit. f. Phys.*, XXXIV) between 40 and 100 μ. The infra-red wave-lengths corresponding to these bands were calculated and found to agree fairly well with the *alternate* lines found in absorption by Czerny as follows:

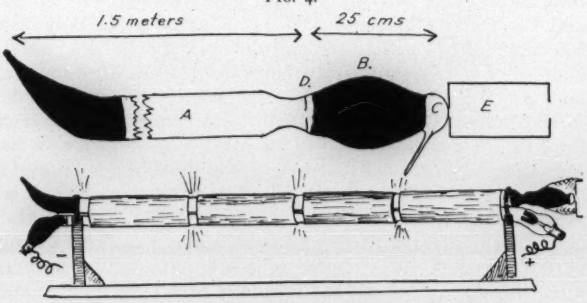
Czerny	Wood
44.1	43.9
48.5	
53.8	53.9
60.4	
68.9	67.1
80.4	
96.0	100.0

Ammonia at atmospheric pressure gave a single line also, for each exciting line. A very sharp triplet excited by Hg 3650, 3654, and 3663, of which the outer lines had wave-lengths of 4157 and 4172. The 4046 line excited a line of wave-length 4672.5. Thus far I have photographed these with the F2 spectrograph only, and the wave-lengths are not very accurate. These lines are identified with the infra-red absorption band at 3 μ.

The ammonia was taken from a commercial iron cylinder and not purified. Coblentz gives this band at 3 μ and it is Band II. of Sir Robert Robertson's recent paper (Proc. R. S. 784, p. 161). No trace of lines corresponding to the strong ammonia bands at 6.5 μ and 10 μ have been observed as yet.

The apparatus for the excitation of the Raman effect in gases consists of a tube of soft glass 5 cm. in diameter and about 150 cm. in length, drawn off into a tapering cone at the rear, and constricted and expanded at the front as shown in the diagram. The lower figure is drawn more nearly to

FIG. 4.



scale, and shows the tube mounted over, and in contact with, a very long Cooper-Hewitt mercury arc lamp of glass. Hollow cylindrical reflectors of very thin highly polished sheet aluminum enclose the two tubes, shutting in all of the light. This is a great improvement on the earlier "light furnaces" described in former papers on iodine fluorescence.

The cylinders were made by wrapping rectangular sheets of the metal around a glass tube of much smaller diameter than that desired, a size being chosen such that the edges of the sheet remained in contact when it expanded by its elasticity.

The cylinders are slipped over the tubes by springing them open with the fingers, and on releasing them they clamp themselves firmly around the two tubes. The upper diagram is not drawn to scale. The bulb *B* is rather longer in proportion to its diameter than is indicated in the figure. This bulb prevents reflexion of light coming from the mirrors and lamp through the diaphragm *D*, against the front wall of the bulb *C*. The preparation of this latter bulb is the most important part of the whole operation. It must be as thin as possible and optically clean, i.e., free from air-bubbles, striæ, or cloudiness. The front wall should not be thicker than thin writing-paper, and if properly made gives almost as clear vision down the tube as a plate-glass window. A window of thin cover glass could be cemented on, in the case of most gases, but I preferred the bulb for the work with HCl.

The diaphragm *D* is a disc of very thin platinum foil, perforated by a hole 4 mm. in diameter, which is as large as can be safely used, as the condition which must be fulfilled is that no part of the lens used for projecting an image of diaphragm on the slit, can "see" any part of the blazing interior of the furnace through the diaphragm. The platinum disc is dropped into position resting against the sloping wall of the constriction (the tube being held vertically), and the glass then melted in spots with a small pointed blast-lamp flame until it takes hold of the platinum. The bulb *B* is then blown, drawing it out during the blowing, and finally the end bulb and exit tube prepared.

The Cooper-Hewitt lamp was mounted on two thin wooden supports in V-shaped notches lined with asbestos board, and the gas-tube held down in contact with it by thin metal bands screwed to the supports and passing over the tubes.

The illumination produced in this way is terrific as the light of the lamp is beaten back and forth between the walls of the reflectors, and, as I have said, it was possible

to photograph the modified line with a five-hour exposure, while the unmodified line comes out with an exposure of only 15 seconds, some of the light in this case coming undoubtedly from the "black cone" and the front wall of the bulb.

The explicit directions for the preparation of the tube, the diaphraming of the light beam and the aiming of the spectrograph will be found in the April number of the *Philosophical Magazine*, 1929.

THE CONDUCTIVITY OF UNI-UNIVALENT SALTS IN CYCLOHEXANOL.

BY

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Research Fellow of the American Scandinavian Foundation.*

INTRODUCTION.

BARTOL RESEARCH FOUNDATION
Communication No. 42.

In this paper will be found some results of conductivity measurements in Cyclohexanol as solvent. This solvent has a comparatively small dielectric constant ($D = 15$ at 25° C.) and a great viscosity ($\eta = 0.595$ at 25° C.), so that the electric properties of the solvent as well as its viscosity are very different from the corresponding properties of water. The measurements were made at concentrations as small as possible (down to concentrations as small as 10^{-5} moles per liter), in the first place to discover if the equivalent conductivity shows proportionality to the square root of the concentration in accordance with the results obtained by Kohlrausch in aqueous solutions at very great dilutions (Kohlrausch's law).

It has been stated before that this relation not only holds for aqueous solutions at great dilutions but also for solvents other than water, i.e., even for solvents whose dielectric constants are smaller than 20.[1] This result is of great interest, as a linear relation between the equivalent conductivity and the square root of the concentration is a consequence of the Debye-Hückel theory for the conductivity of electrolytes. As is well known, this theory is built up on the assumption of complete dissociation even at finite concentrations and it attempts to explain the decrease of the equivalent conductivity at increasing concentrations, by taking into account the obstruction caused by the interionic forces. According to the Debye-

* Investigation conducted at the Bartol Research Foundation of the Franklin Institute.

[1] Lee H. Hartley and R. P. Bell, *Transactions of the Faraday Soc.*, Vol. XXIII, 1927, p. 396.

Hückel theory and the same theory as improved by Onsager we have $\Lambda_\gamma = \Lambda_0 - \alpha\sqrt{\gamma}$, at small concentrations. Λ_γ and Λ_0 are the equivalent conductivities at the concentration γ and at infinite dilution respectively. The slope of the line representing the connection between Λ_γ and the square root of the concentration according to the Debye-Hückel theory, is indefinite as α contains the mean diameter of the ions as an unknown quantity.

According to Onsager on the other hand it is possible to calculate the slope α of the curve Λ_γ vs. γ whereby a comparison with the value experimentally determined becomes possible. Such a comparison is of special interest with non-aqueous solutions having a small dielectric constant, as in such cases deviations from the theory may be expected rather than in aqueous solutions on account of association and approximations made in the theory.

SOLVENT AND SALTS.

Cyclohexanol (from Pulenc Frères, Paris) was twice distilled at about 2–3 mm. mercury pressure. The first fraction contained small quantities of water.

According to previous measurements, the freezing point of the main fraction in the second distillation could not be raised appreciably by further distillations. In these measurements, therefore, the main fraction of the second distillation was used for the conductivity measurements.

Measurements were performed with the following salts: lithium chloride, lithium bromide, lithium perchlorate and guanidine nitrate.

A preparation of lithium chloride from Backer was used in the first series. The salt was dried at about 160° C. until the weight was constant. In the second series a preparation from Poulenc Frères was used. The lithium chloride used for the second series was dissolved in alcohol (absolute) and Li_2CO_3 was added to the solution. After filtering, the solution was evaporated on a water bath and then heated in a platinum crucible until the salt was thoroughly melted. After cooling the same procedure was repeated. The pulverised salt was at last heated 12 hours in a drying-oven at about 160° C. until the weight was constant.

The other salts used in the conductivity measurements were the same samples employed previously in freezing point measurements. Information regarding the purification of lithium bromide, lithium perchlorate and guanidine nitrate will be found in a paper by E. Schreiner and the author in *Zeitschrift für physikalische Chemie*, Vol. 124, p. 1, and in a paper at present in publication in the *Philosophical Magazine*. It will suffice to note here, that, in cases where the salts contained water of crystallization, this was removed and the salts carefully dried until the weight was constant before making up the standard solution.

THE CONDUCTIVITY CELL.

Since the specific conductivity of the solvent was very small—of the order 10^{-9} cm.$^{-1}$ ohm^{-1}—it was necessary to use a cell with a small cell constant ($c = 0.01622$ cm.). Although this one was very small the resistance of the cell filled with solvent was of the order of 10^7 ohms. The cell had electrodes 2 mm. apart. The diameter was about 4 cm., and the electrodes were coated with gray platinum.

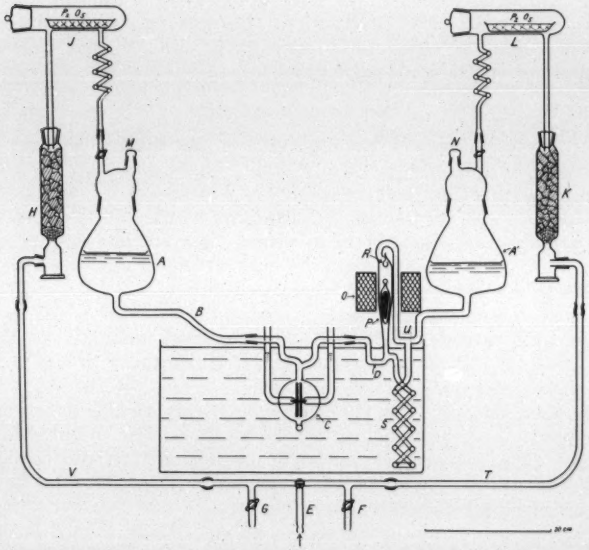
It is evident that under these circumstances, small impurities from the electrodes will have great influence on the resistance. It also appeared that the resistance of the cell containing cyclohexanol and solutions in this solvent did not remain constant. On the other hand it was possible to attain constancy of the resistance by letting the solvent or the solution pass continuously through the cell, so that the liquid between the electrodes was constantly renewed. The apparatus used is represented in Fig. 1.

The cell C was immersed in an electrically heated bath whose temperature was kept constant to 0.01° C. by a thermoregulator filled with xylol and distilled mercury. The bath was filled with transformer oil. The cell communicated with two flasks (capacity 500 c.c.) A and A' by the tubes B and DU.

The system was filled at the beginning of each run with the pure solvent. The flasks A and A' were connected through the tubes $JHVE$ and $LKTE$ with the pressure pump. By aid of the three-way tap at E the right or the left side could be put under pressure. If for instance one put the right side under

pressure and connected the left side by the tap *G* with the air, the liquid passed through the system from right to the left. During the measurements of the resistance in the cell the solvent (or solution) passed slowly through the spiral *S* before passing through the cell. In this way the liquid attained the temperature of the bath. Parallel with the spiral

FIG. 1.



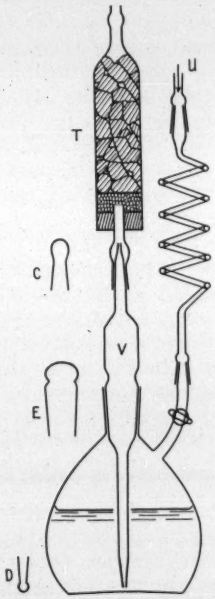
was connected a glass tube *URP* of greater dimensions yielding less resistance to the liquid than the spiral. This connection could be opened or closed by a stopcock of special construction as will be seen by the figure. The stopcock *P* containing a piece of iron could, by the help of the solenoid *O*, be lifted upon the hook *R*, whereby communication was obtained through the spiral as well as through the tube *DPRU*.

After a new portion of a standard solution had been added to the bottle *A* it was necessary to force the liquid from one

side to the other about 10 times before the solution became homogeneous. On account of the great viscosity of the solvent and the small diameter of the spiral it would have taken too long to get a homogeneous solution without using the by pass *PRU* above described. During the measurement of the resistance of the cell, however, the connection *DPRU* was closed.

In order to exclude moisture from the air circulating to the bottles *A* and *A'*, the tubes *HJLK* containing $CaCl_2$ and P_2O_5 were connected with the system as shown in the figure.

FIG. 2.



PREPARATION OF THE SALT SOLUTION.

The standard solution was made up in a bottle (Fig. 2) of 500 c.c. capacity with the same sample of cyclohexanol that

was used for filling the cell and the two bottles A and A'. Weighed quantities of dried salt were transferred to the bottle containing the amount of pure cyclohexanol needed to give a solution approximately of a concentration between 0.01 and 0.06 moles per liter, after which the flask was rotated and heated to about 40° C. until the salt was dissolved. The stopper E was then replaced by the weight pipette V, which was filled by applying suction on the drying tube T. The tube U was put into communication with a tube containing P_2O_5 in order to prevent moisture from getting into the bottle. During the weighing the stoppers C and D were put on the pipette.

The concentrations are expressed in gram equivalents per liter. For the purpose of converting the concentrations in weight normalities to volume normalities it is necessary to know the density of the solution. The greatest concentrations being only about 0.001 mole per liter, the density of the solution is sensibly the same as that of the pure solvent. For this reason the density of the pure solvent $d = 0.9485$ gram per c.c. at 25° C. was used in computing the volume concentration.

MODE OF PROCEDURE.

First of all the resistance of the cell filled with the solvent was measured. Then salt solution was added to the bottle A (Fig. 1) through the cap M from the weight pipette, while a slow stream of dry air was passed into the bottle. After having made the solution homogeneous in the manner above described, the resistance was measured. Then a new portion from the salt solution was added and so on. In this way, in each run the conductivity was measured at increasing concentrations.

MEASUREMENTS OF RESISTANCE.

The resistance of the cell was measured in a Wheatstone bridge with alternating current supplied by an oscillator giving a frequency of 1,000 cycles per. sec.[2] By the aid of two switches, a two tube amplifier and a filter permitting only

[2] The oscillator and the amplifier were designed by Dr. W. Nottingham and made under his supervision in the workshop of the Bartol Research Foundation. I am most grateful to Dr. Nottingham for having given me the opportunity to use this equipment for my measurements.

1,000 cycles a second to be transmitted could be put in series with the telephone, or the telephone could be employed without any amplifier. The grounding was established in a manner employed by G. Jones and R. C. Josephs. Without connecting the telephone direct to earth it is possible to obtain the same effect with the arrangement employed by Jones and Josephs and described fully in their paper.[3] The bridge assembly was of the normal Wheatstone type, with a cylindrical bridge drum which could be prolonged by resistances at each end in order to get greater accuracy. The resistances were of the special non-inductive type. The Kohlrausch bridge drum as well as the resistance boxes were calibrated at Leeds and Northrup at 1,000 cycles. In order to be able to compensate for the capacity of the cell a variable condenser was put in, parallel to the resistance boxes. By the device described it was possible to obtain a sharp minimum in the telephone.

THE CELL CONSTANT.

The cell constant was determined 4 times during the work by measuring the resistance of the cell, first filled by twice distilled water, and then by a potassium chloride solution. The equivalent conductivity of the aqueous potassium chloride has been computed by Kohlrausch and Maltbyes formula for the equivalent conductivity at 18° C. $\Lambda_{18} = 129.91 - 80.75\sqrt{\gamma}$; γ is the concentration expressed in moles per liter.

The equivalent conductivities computed in this way were compared with values obtained by interpolation of measurements of the equivalent conductivity of potassium chloride in water by Wieland. The divergencies between the values found in the two different ways were within one part in one thousand.

The specific conductivity at 25° C. has been calculated from the values at 18° C. by the help of the formula given in Landolt-Börnstein's Physikalisch Chemische Tabellen for potassium chloride:

$$k_t = k_{18}[1 + c(t - .18) + c'(t - 18)^2] \qquad \begin{matrix} c = 217 \times 10^{-4} \\ c' = 67 \times 10^{-6} \end{matrix}$$

[3] Dr. Josephs kindly gave me information upon this method of grounding the bridge. The paper by Jones and Josephs was recently published in *Journal of the Amer. Chem. Society*, Vol. 50, 1928, p. 1049.

The cell constant c was calculated from the equation:

$$k_\gamma = c\left(\frac{1}{r_i} - \frac{1}{r}\right); \qquad c = k_\gamma \frac{r r_i}{r - r_i}.$$

Here r and r_i are the resistances of the water and the solution respectively and k_γ the specific conductivity of the solution.

All measurements were made at 25° C.

The values for the cell constant obtained are tabulated below:

TABLE 1.

Date.	Concentration in Moles/liter.	Cell Constant.
Jan. 4, 1928	0.001020	0.01629
" 11, 1928	0.0009061	0.01624
Feb. 22, 1928	0.0004236	0.01610
" 22, 1928	0.000936	0.01626

The mean value used for the cell constant is 0.01622.

THE VISCOCITY OF CYCLOHEXANOL.

The friction coefficient, η, was measured by a viscometer of the type described in Ostwald Luther's "Physico-Chemische Messungen," 3. ed., 1920, Fig. 153. Special care was taken in order to avoid moisture getting into the apparatus. The apparatus was calibrated by a 60 per cent. sugar solution, and a series of measurements made at different temperatures.

Besides my own measurements in Table 2 will be found also the results from measurements made by Dr. R. W. Williamson in his laboratory in the Chemical Department of the experimental station of the Du Pont Company—in Wilmington, Del.[4]

TABLE 2.

Temperature.	η.	ηmean.	
25.0	0.600	0.596	Williamson
25.0	0.592		Frivold
26.02		0.549	Frivold
30.0	0.421 *	0.424	Williamson
30.02	0.426		Frivold

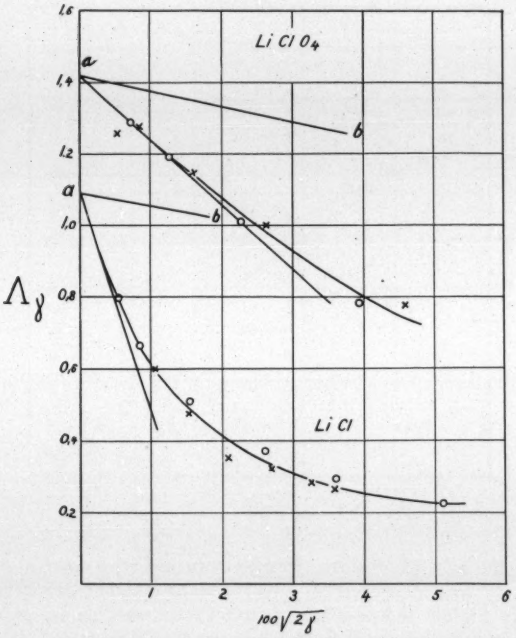
* Mean of results obtained by two different apparatus 0.406 and 0.436. The difference is probably due to moisture in the apparatus.

[4] It is with gratitude that I remember Dr. Williamson's kindness in making the measurements for me.

RESULTS OF MEASUREMENTS.

In the following set of tables is given in Column 1 the concentration expressed in moles per liter, in Column 2 the square root of the ionic concentration, in Column 3 the resistances of the solution, in Column 4 the specific conductivity of the salt

FIG. 3.



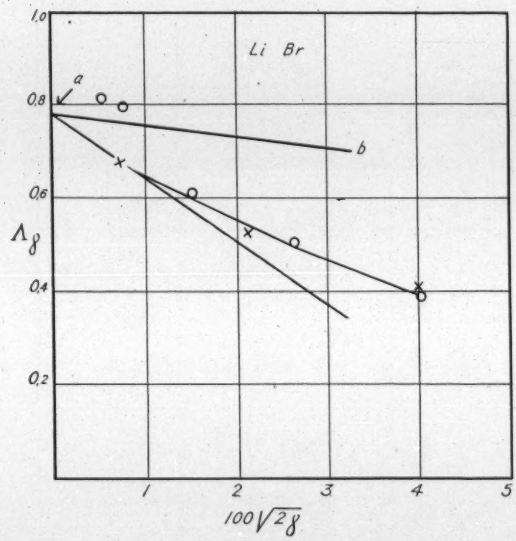
and in Column 5 the equivalent conductivity. The specific conductivity of the salt, k_γ is the difference between the same quantities for the solution and the solvent.

$$k_\gamma = c\left(\frac{1}{r_i} - \frac{1'}{r'}\right),$$

where c is the cell constant, r_i and r are the resistances of the solution and the solvent respectively. At the head of each series will also be found the specific conductivity $k_s = c/r$ of the solvent.[5]

The measurements were made at 25° C.

FIG. 4.



In the case of lithium chloride solution, the specific conductivity was measured for two different concentrations at a slightly higher temperature 34.95° C. as well as at 25° C. The temperature coefficients computed will be found at the end of Table 3.

In Figs. 3, 4 and 5 the equivalent conductivity (given in the above tables) is plotted against the square root of the con-

[5] It should be noted that the specific conductivity of the solvent used for the guanidine nitrate solutions is abnormally high. But another series of measurements could not be made on account of lack of time.

centration. The curves are extrapolated to infinite dilution in order to find the equivalent conductivity Λ_0 at that limit.

FIG. 5.

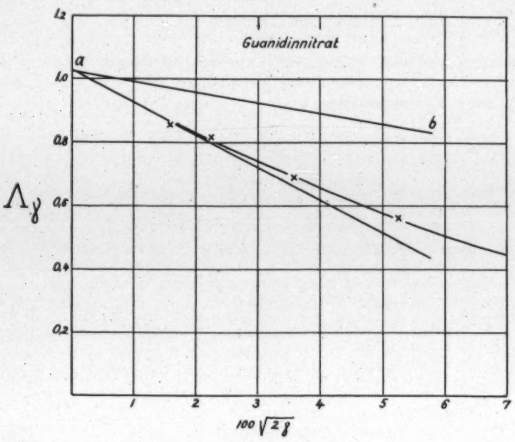


TABLE 3.

LiCl in $C_6H_{11}OH$

$\Lambda_0 = 1.09$.

$r = 8.78.10^6$ ohms, $k = 1.847 \cdot 10^{-9}$, $t = 25°$ C.

$\gamma.10^4$.	$100\sqrt{2\gamma}$.	r_i.	$k\gamma.10^9$.	$\Lambda\gamma$.
0.5424	1.042	472500	32.48	0.599
1.1415	1.51	290560	53.98	0.473
2.1505	2.074	210200	75.32	0.350
3.6370	2.697	136800	116.71	0.321
5.2781	3.246	107700	148.76	0.282
6.3505	3.564	95120	168.67	0.266

Second Series.

$r = 8.82.10^6$ ohms, $k = 1.839 \cdot 10^{-9}$, $t = 25°$ C.

$\gamma.10^4$.	$100\sqrt{2\gamma}$.	r_i.	$k\gamma 10^9$.	$\Lambda\gamma$.
0.1441	0.537	1215320	11.51	0.799
0.3589	0.847	630400	23.89	0.666
1.166	1.531	264860	59.40	0.509
3.363	2.593	128120	124.76	0.371
6.421	3.584	85140	188.67	0.294
13.07	5.103	54760	294.36	0.225

$r = 6.28.10^6$ ohms, $k = 2.59 \cdot 10^{-9}$, $t = 34.95°$ C.

$\gamma . 10^4$.	$100\sqrt{2\gamma}$.	r_i.	$k\gamma 10^9$.	$\Delta\gamma$.
1.166	1.531	178680	88.19	0.755
13.07	5.103	39405	409.03	0.313

The mean temperature coefficient in the interval of temperature 25° C. to 35° C. at the concentrations 0.0001166 and 0.001307 mol per liter are computed to 0.0394 and 0.0385 respectively.

TABLE 4.

LiBr in $C_6H_{11}OH$.

$\Lambda_0 = 0.79$.

$r = 6.82.10^6$ ohms, $k = 2.378 \cdot 10^{-9}$, $t = 25°$ C.

$\gamma . 10^4$.	$100\sqrt{2\gamma}$.	r_i.	$k\gamma 10^9$.	$\Delta\gamma$.
0.1275	0.505	1276000	10.33	0.811
0.2823	0.751	652400	22.48	0.797
1.097	1.481	236800	66.12	0.603
3.426	2.618	93388	171.30	0.500
8.041	4.010	51535	312.36	0.389

Second Series

$r = 1.01.10^6$ ohms, $k = 16.08 \cdot 10^{-9}$, $t = 25.02°$ C.

$\gamma . 10^4$.	$100\sqrt{2\gamma}$.	r_i.	$k\gamma 10^9$.	$\Delta\gamma$.
0.2743	0.741	464000	18.88	0.688
2.267	2.129	121000	117.96	0.520
7.933	3.984	48400	319.04	0.402

TABLE 5.

$LiClO_4$ in $C_6H_{11}OH$.

$\Lambda_0 = 1.42$.

$r = 4.35.10^6$ ohms, $k = 3.727 \cdot 10^{-9}$, $t = 25°$ C.

$\gamma . 10^4$.	$100\sqrt{2\gamma}$.	r_i.	$k\gamma 10^9$.	$\Delta\gamma$.
0.1381	0.526	772500	17.27	1.251
0.3540	0.841	331700	45.17	1.276
1.328	1.629	104000	152.23	1.146
3.395	2.606	47400	338.46	0.997
10.45	4.572	19940	809.71	0.775
35.25	26.55	1578	102.74	0.291

Second Series.

$r = 2.15.10^6$ ohms, $k = 7.53 \cdot 10^{-9}$, $t = 25°$ C.

$\gamma . 10^4$.	$100\sqrt{2\gamma}$.	r_i.	$k\gamma 10^9$.	$\Lambda\gamma$.
0.2647	0.728	390750	33.98	1.284
0.7944	1.261	158700	94.68	1.192
2.593	2.277	60015	262.74	1.013
7.737	3.933	26368	607.61	0.785

TABLE 6.

Guanidin Nitrate in $C_6H_{11}OH$.

$\Lambda_0 = 1.03$.

$r = 0.491.10^6$ ohms, $k = 33.07 \cdot 10^{-9}$, $t = 25°$ C.

$\gamma . 10^4$.	$100\sqrt{2\gamma}$.	r_i.	$k\gamma 10^9$.	$\Lambda\gamma$.
0.2833	0.753	326800	16.57	0.585
1.278	1.597	113800	109.46	0.857
2.476	2.225	69100	201.66	0.815
6.362	3.567	34335	439.33	0.691
13.726	5.239	20081	774.65	0.564
94.24	13.73	5450	2943.00	0.312

DISCUSSION OF THE RESULTS OBTAINED.

From the graphical representation it will be seen that there does not exist a linear relation between the equivalent conductivity and the square root of the concentration for the three lithium salts between the concentrations 0.00001 and 0.001 mole per liter. However for guanidine nitrate the law of Kohlrausch seems to hold at very small concentrations. That more of the lithium salts do not obey this relation or do so only at exceptionally high dilutions has also been observed in other non-aqueous solvents. The peculiar manner in which most of the lithium salts behave is probably due to the formation of complex ions even in dilute solutions.

But even if the relation of Kohlrausch does not hold for the concentrations here measured, according to Onsager's theory one may expect that the curves extrapolated to infinite dilutions will have tangents coinciding with those calculated from the theory.

According to Onsager we have, for uni-univalent salts

1) $$\Lambda_\gamma = \Lambda_0 - \alpha\sqrt{2\gamma};$$

where

$$\alpha = \frac{5.78 \cdot 10^5}{(DT)^{3/2}} \Lambda_0 + \eta \frac{58.0}{(DT)^{3/2}}$$

and where Λ_γ and Λ_0 are the equivalent conductivities at the concentration γ and at infinite dilution. γ is the concentration in moles per liter, D and η are the dielectric constant and the friction coefficient of the solvent, and T the absolute temperature. The first term in α arises from the additional electric field caused by the ionic atmosphere, the second term arises from electrophoresis.

For cyclohexanol $D = 15.0$, $\eta = 0.595$ at $T = 298°$ abs., and

$$\alpha = 1.93\Lambda_0 + 1.46, \Lambda\gamma = \Lambda_0 - \alpha\sqrt{2\gamma}.$$

Λ_0 for the four salts has been found by extrapolation and their values are tabulated below together with α.

TABLE 8.

	Λ_0	$\alpha = 1.93\Lambda_0 + 1.46$.
Lithium chloride	1.09	3.56
Lithium bromide	0.79	2.98
Lithium perchlorate	1.42	4.20
Guanidin nitrate	1.03	3.45

On the basis of the values tabulated for Λ_0 and α the lines *ab* in Figs. 3, 4 and 5 representing the limiting law have been computed. It will be seen that there exists a great deviation between the lines representing the limiting law and the tangents to the curves extrapolated. This is very remarkable. For even if the association is noticeable even at very small concentrations and in this way induces greater deviations from Λ_0 than expected according to the theory, the same theory requires that formula 1 should hold as a limiting law. Because at infinite dilution the effect of the association will tend towards zero in proportion to the effect of the ionic atmosphere.

In fact, the possibility exists that the conductivity curve below concentrations of 10^{-5} moles per liter bends towards the left side with decreasing concentrations. Onsager has shown this to be the case for some aqueous solutions and has found agreement between this theory and the experiments, taking into account the effect mentioned. The experimental curves

in this case however do not show any inversion tangents and as even no support can be found that the equivalent conductivity at infinite dilution is less than those found by extrapolation, the question of the existence of a discrepancy between the experiments and the theory has not been solved.[6]

If we assume that at infinite dilution the motion of the ions obeys Stokes' law a "mean" radius of the ions can be calculated from the equation

$$\text{Force} = \text{velocity} \times 6\pi\eta r, \tag{2}$$

where η is the friction coefficient.

If L_0 is the mobility of the ion at infinite dilution, equation 2 becomes:

$$L_0 = \frac{N\epsilon^2}{9 \cdot 10^{11} \cdot 6\pi\eta r}.$$

N = Loschmids number = $6.06 \cdot 10^{23}$,
$\epsilon = 5.774.10^{-10}$ E.S.U.

For a uni-univalent salt we have:

$$\Lambda_0 = \frac{N\epsilon^2}{9 \cdot 10^{11} \cdot 6\pi\eta}\left(\frac{1}{r_1} + \frac{1}{r_2}\right),$$

or

$$r_{\text{mean}} = \frac{16.30 \cdot 10^{-9}}{\eta \cdot \Lambda_0}.$$

In the following table η, Λ_0 and r_{mean} are calculated for 4 uni-univalent salts.

TABLE 9.

	$\eta . \Lambda_0$	$r_{\text{mean}} \cdot 10^8$ cm.
LiCl	0.648	2.52
LiBr	0.470	3.47
$LiClO_4$	0.845	1.93
$CNH(NH_2)_2 \cdot HNO_3$	0.613	2.65

[6] In this connection mention should be made of the fact that E. Schreiner, F. Ender and the author have performed freezing point measurements with the same uni univalent salts in the same solvent. (*Zeitschrift für physikalische Chemie*, Vol. 124, 1926, p. 1.) According to these measurements there seems to be good agreement between the Debye-Hückel Theory for the osmotic phenomena and the experiments. As is well known this theory is built up on the same assumptions as the conductivity theory. It has to be remembered however that the freezing point depressions could not be measured at greater dilutions than 0.001 mole per liter.

It will be seen from the table that the values of r calculated are of the right magnitude.

SUMMARY.

1. Conductivity measurements have been performed for LiCl, LiBr, $LiClO_4$ and Guanidin nitrate in Cyclohexanol as solvent at concentrations between 0.00001 and 0.001 mole per liter. The equivalent conductivity is found by extrapolating.

2. The temperature coefficient of the specific conductivity is determined for LiCl at two concentrations.

3. The viscocity of cyclohexanol has been measured at different temperatures.

4. The square root relation of Kohlrausch was found to hold for guanidine nitrate only.

5. No agreement was found between the experiments and the Debye-Onsager theory.

The conductivity measurements were performed more than a year ago while I was a Research Fellow of the Bartol Research Foundation and of the American-Scandinavian Foundation.

I am very indebted to Dr. W. F. G. Swann, the Director of Bartol Research Foundation, for the interest he has taken in this work. At the same time I also want to express my gratitude to the Board of the Bartol Research Foundation for giving me the opportunity to perform this work at the Laboratories of the Foundation.

DEPARTMENT OF PHYSICS,
UNIVERSITY, OSLO,
June, 1929.

PROPAGATION OF DETONATION ACROSS A GAS-GAP BETWEEN TWO CARTRIDGES OF EXPLOSIVE[1]

BY

G. St. J. PERROTT[2] and D. B. GAWTHROP.[3]

THIS paper presents part of a study of the sensitivity of mining explosives to detonation, a property that is usually expressed in terms of the distance across which detonation will propagate from one cartridge to another separated from it by an air-gap. A previous article[4] gave data which show the velocity of propagation of the disturbance in an air-gap. It was shown that the velocity is a function of the rate of detonation of the explosive, but the disturbance in the gap often travels faster than the detonation wave in the explosive. This was most noticeable in the case of explosives having a comparatively low rate of detonation—that is, a rate of about 2,000 m. per second. Here the velocity over the first few centimeters of air-gap was as high as 3,000 m. per second. This phenomenon was first noted by Laffitte[5] in experiments with charges of explosives contained in glass tubes.

There is as yet some doubt as to whether the second cartridge is detonated by a shock wave sent out from the initiating cartridge or whether the hot expanding gases (perhaps still reacting) physically move across the gap and, by their impact on the second cartridge, cause it to detonate. The present experiments were undertaken in the hope of throwing further light on the mechanism of transfer of detonation across a gap.

[1] Published with permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

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[4] Perrott, G. St. J., and Gawthrop, D. B., "Propagation of Detonation across an Air-gap between Two Cartridges of Explosive," JOUR. FRANK. INST., Vol. 203, 1927, pp. 387–406.

[5] Laffitte, P., "Recherches experimentales sur l'onde explosive et l'onde de choc," *Annales des Physiques*, Vol. 4, 1925, pp. 587–694; also *Compt. Rend.*, Vol. 176, 1924, pp. 1277–1279.

WORK OF PREVIOUS INVESTIGATORS.

Vieille[6] employed a fulminate detonator to produce shock waves in a tube 1.27 m. in length and 22 m.m. in diameter. The speed of the wave was measured by means of small pistons at each end of the tube, and the movements of these were recorded on a revolving smoked drum. Experiments were made with air, hydrogen, and carbon dioxide at atmospheric pressure and at elevated and reduced pressures. Vieille concluded from the experiments that for these waves—

1. At the same pressure, the law of densities[7] relative to the propagation of sound is only approximately followed and this effect appears diminished. However, the considerable variations of speed caused by different media suffice to show that the phenomenon studied is certainly one of propagation and not merely of physical movement of the gaseous products of explosion.

2. The influence of pressure, of no effect in the case of a propagation of sound, is very important in the case of propagation of a discontinuity. Increase of pressure lowers the speed of propagation from the value at atmospheric pressure which is 2 to 3 times as great as that of sound, to a value close to the speed of sound when the pressure is raised to 21–23 atmospheres.

Results were as follows:

	Hydrogen.	Air.	Carbon Dioxide.
Density	1	14	22
Velocity of sound, m./sec.	1,319	340	281
Velocity of propagation of discontinuity, m./sec.: Pressure, atm.			
0.01	....	1,577	...
1	2,104	1,041	814
21–23	1,555	576	363

[6] Vieille, M., "Etude sur le rôle des discontinuites, Memorial des Poudres et Salpêtres," Vol. 10, 1899, pp. 177–260.

[7] $V = \sqrt{\frac{KP}{\rho}}$, where V = velocity of sound at a given temperature, $K = \frac{C_p}{C_v}$, P = pressure, and ρ = density of the gaseous medium.

Vieille believed that propagation of the detonation wave through an explosive mixture of gases was a phenomenon of the same type. Chapman[8] and Jouguet[9] have developed the theory of propagation of detonation in gaseous mixtures, in which the explosion wave is regarded as a wave of compression in a medium which is discontinuous in the vicinity of the wave front.

Becker[10] photographed the detonation of charges of explosive on a moving film and showed photographs of the "flame" of the explosive moving at a rate faster than that of the detonation wave in the explosive, but he did not comment on the fact; he believed the flame to be reacting gases.

Laffitte[5] investigated the speed of the disturbance in an air-gap by means of a photographic method. He employed glass tubes 6 to 7 mm. in diameter and 75 cm. in length. The dynamite, packed to a density of 0.95 g. per c.c., occupied a length of about 25 cm. at one end of the tube. When the detonation of this charge was photographed on a moving film it was found that in addition to the record produced by the detonating dynamite, a luminous phenomenon was recorded in the part of the tube which was occupied by air. The speed of this luminous disturbance at first was 4,000 m. per second but diminished to about 2,000 m. at the time when the disturbance ceased to be recorded. With a tube 13 mm. in diameter the disturbance was visible over some 60 cm. and its initial velocity was 7,000 m.; the final velocity was again about 2,000 m. In 6-mm. tubes, increasing the charging density from 0.80 to 0.95 g. per c.c. increased the length over which the shock wave was visible but did not affect its speed. The character of the phenomenon was also independent of the length of the charge if this was several times the diameter of the tube. The effect was the same in CO, CO_2, SO_2, N_2O, and NO_2. In hydrogen, while the length of the luminous disturbance was the same as in air, its speed was almost uniform at about 5,000 m. per second. Reduction of pressure in air

[8] Chapman, D. L., "Rate of Explosion in Gases," *Phil. Mag.*, Vol. 47, 1899, pp. 90–104.

[9] Jouguet, E., "Mecanique des Explosifs," Paris, 1917.

[10] Becker, R., "Physikalisches über feste und gasförmige Sprengstoffe," *Zt. für Technische Physik*, Vol. 7, 1922, pp. 152–159; 249–256.

at first increased the length over which the phenomenon was visible and then reduced the length. Results were as follows:

Pressure, mm. of Hg	Length, cm.
0.04	2
0.1	4
3	10
7	40
25	60
50	70
120	75
300	30
760	28

At the low pressures, the speed tended to be constant until the phenomenon was no longer visible; for example, at a pressure of 6 mm. of Hg the speed was 5,000 m. per second over a length of 40 cm. Laffitte concluded that he was dealing with a luminous pressure wave and not with physically moving reacting gases or hot solid particles.

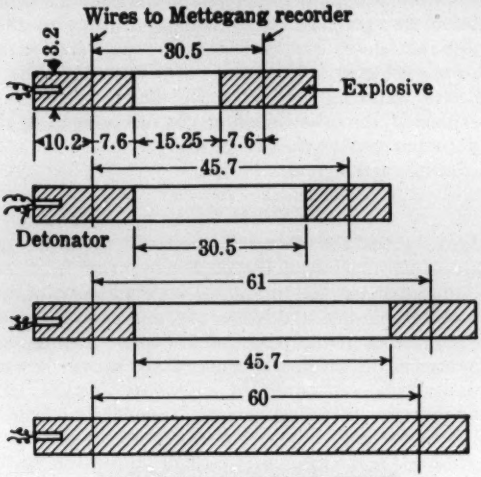
EXPERIMENTAL PROCEDURE.

MEASUREMENTS OF VELOCITY BY METTEGANG RECORDER.

The experimental procedure of the writers consisted simply in repeating the experiments described in a previous article,[4] but with either air, hydrogen, or carbon dioxide in the gap between the two cartridges, which were wrapped in paper as in the previous experiments. Figure 1 shows the arrangement of cartridges and gaps. The two wires threaded through the explosive led to the Mettegang recorder where the time-interval elapsing between the breaking of the two wires by the detonation of the explosive was recorded on a smoked revolving drum. By means of small glass tubes, one of which was cemented to the paper wrapper at the initiating end of the gap and the other to the paper wrapper at the receiving end of the gap, gas was passed into and through the gap, from a tank under pressure, for two minutes before the explosive was fired.

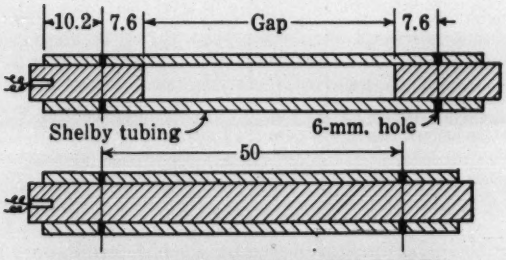
Similar experiments were also made in Shelby steel tubes with air in the gap. The tubes had an internal diameter of 3.5 cm. and a wall 0.6 cm. in thickness. Velocities were measured by means of the Mettegang recorder in the same manner as employed with the charges in paper tubes.

FIG. 1.



CHARGES IN PAPER TUBES

Dimensions are in centimeters



CHARGES IN SHELBY STEEL TUBES

Arrangement of explosive charges.

MAXIMUM DISTANCE OF PROPAGATION.

Tests were also made to determine the distance over which detonation was propagated from one cartridge to the other with different gases in the separating gap and with three samples of explosive. Two series of tests were made, one in which both initiating and receiving cartridges were of the same explosive, the other in which the receiving cartridge was always 40 per cent. straight nitroglycerin dynamite, while the initiating cartridge was varied.

EXPLOSIVES USED.

Table 1 gives the chemical analysis, apparent density, and rate of detonation of the explosives used in the experiments. Explosives No. 10 and 14 were 40 per cent. straight nitoglycerin dynamite, and No. 11, 12, and 13 were ammonium nitrate explosives of the permissible type. Numbers 11 and 13 had rates of detonation of about 2,800 m. per second, No. 12 a rate of 2,000 m., and No. 10 a rate of 4,600 m. when confined in paper tubes.

TABLE 1.

Properties of Explosives Used in Experiments.

Explosives No.	10	11	12	13	14
Chemical analysis, per cent.:					
Moisture	0.7	0.6	0.5	1.0	1.1
Nitroglycerin	39.3	—	—	—	—
Nitroglycerin and nitroglycol	—	9.4	10.5	9.7	39.6
Ammonium nitrate	—	75.5	75.1	75.3	—
Sodium nitrate	43.8	3.2	4.6	4.7	43.9
Calcium carbonate	0.6	0.7	0.2	0.2	1.0
Carbonaceous combustible material	15.35	10.6	9.1	9.1	14.4
Apparent density, g./c.c.	1.32	0.94	0.82	0.85	—
Rate of detonation, m./sec.	4,610	2,780	2,030	2,890*	5,140*

* Determination made in Shelby steel tube.

METHOD OF CALCULATING VELOCITY IN THE GAP

In the experimental procedure, each determination measured the time that elapsed between the instants of breaking of each of two wires, one of which was threaded through the explosive on the initiating side of the gap and the other

through the explosive on the receiving end of the gap. (See Fig. 1.) This method was followed rather than that of placing the wires in the gas-gap itself, because it was found that unsatisfactory records were obtained with the latter procedure. Hence, each determination included the time of propagation of detonation over about 15 cm. of explosive as well as that over the gas-gap. In calculating speeds over the gap it was necessary to make correction for the time occupied by the detonation wave in traversing the 15 cm. of explosive.

To make this correction, the velocities of propagation over explosive and gas-gap were plotted against the length of the gap, and a smooth curve was drawn through the points. The time taken for the impulse to travel from the first to the second wire was then calculated from this curve. The time taken for the disturbance to pass across the gap was obtained by subtracting the time required for detonation of the length of explosive included between the wires. (See column 5, Table 3.) The reciprocal of this time in seconds multiplied by the length of the gap in meters gives the average velocity across the gap in meters per second. This velocity is close to the "instantaneous" velocity or velocity in the wave-front for small gaps, but for the longer gaps it is obviously an average of high velocities at the beginning and lower velocities at the end of the gap. To obtain figures giving an idea of the instantaneous velocity, the time taken for the disturbance to pass over a given gap is subtracted from the time over the next longer gap, thus giving the time over a small increment of gap, usually 15 cm. In this manner the figures in column 6, Table 3, were calculated. From column 6 the "instantaneous" velocity, or average velocity over each 15-cm. increment of gap, was calculated.

This method is based on several assumptions which may not be entirely justified—namely, that:

1. The rate of detonation of the explosive on each side of the gap is the same as the average rate determined over a 60-cm. column of explosive. (See Fig. 1.)

2. There is no time lag between the instant at which the disturbance reaches the second cartridge and the instant at which it detonates.

3. The velocity over, say, the first 30 cm. of gap is the same whether the cartridges are 30 cm. or 60 cm. or more apart.

From such data as we have available, assumptions 1 and 3 seem to be justified, but there is distinct evidence that assumption 2 is not always justified, as is brought out later from photographs of the phenomenon.

Results of Tests.

Table 2 contains the original data. A few experiments were made with helium in the gap. The figures for rate of detonation are the average rate over the gap and about 15 cm. of explosive which was also included between the wires.

Table 2.

Average Rate of Detonation of Two Cartridges of Explosive Separated by a Gas-gap.

Length of Gas-gap, Cm.	15.25	30.5	45.7	61.0	76.2	91.5	106.7	121.9	137.2
Av. rate of detonation between wires (explosive plus gap):									
Explosive No. 10									
Hydrogen...	5,040	5,370	5,530	5,250	5,230	4,840	4,580	3,320	2,240
Air.....	4,590	4,470	4,080	3,660	3,160	2,270	1,990	1,100	
Carbon dioxide.....	4,350	3,970	3,420	3,010	2,510	2,000			
Helium.....	—	5,200							
Explosive No. 11									
Hydrogen...	3,720	4,050	3,900	3,510	3,010	2,020			
Air.....	3,500	3,200	2,690	2,180	1,620				
Carbon dioxide.....	3,230	2,860	2,190	1,860					
Helium.....	3,730	4,130							
Explosive No. 12									
Hydrogen...	2,960	3,150	3,310	3,300	3,230	2,930	1,750		
Air.....	2,760	2,750	2,530	2,130	1,550	1,280			
Carbon dioxide.....	2,670	2,340	2,030	1,260					

Table 3 shows the method of calculating the instantaneous velocity in the gas-gap for one of the test series in which hydrogen was employed in the gap and explosive No. 10 used as the initiator of the disturbance in the gap. Table 4 and Figures 2, 3, and 4 show the calculated instantaneous velocities obtained with explosives No. 10, 11, and 12 over

TABLE 3.

Method of Calculating Velocity of Propagation of Disturbance in a Hydrogen Gap for Explosive No. 10.

1	2	3	4	5[a]	6[b]	7[c]	8
Distance between Wires, Cm.	Length of Gas-Gap, Cm.	Velocity, m./sec.		Time over Explosive plus Gap, Seconds	Time over Whole Gap, Seconds	Time over Increment of Gap, Seconds	Instantaneous Velocity, m./sec.
		Measured	From Smooth Curve				
				$\times 10^{-4}$	$\times 10^{-4}$	$\times 10^{-4}$	
30.5	15.25	5,040	5,040	0.605	0.274	0.274	5,560
45.7	30.5	5,370	5,370	0.851	0.520	0.246	6,200
61.0	45.7	5,530	5,530	1.103	0.772	0.252	6,050
76.2	61.0	5,250	5,460	1.395	1.064	0.292	5,220
91.5	76.2	5,230	5,260	1.740	1.409	0.345	4,420
106.7	91.5	4,840	4,930	2.163	1.832	0.423	3,610
121.9	106.7	4,580	4,480	2.722	2.391	0.559	2,730
137.2	121.9	3,320	3,820	3.585	3.254	0.863	1,770
152.5	137.2	2,240	2,240	6.800	6.469	3.215	470

[a] Time taken for detonation to travel over length of explosive between the wires (see Fig. 1) = 0.331×10^{-4} sec.

[b] Reciprocal of column 6 × length of gap in meters gives rate over whole gap in m./sec.

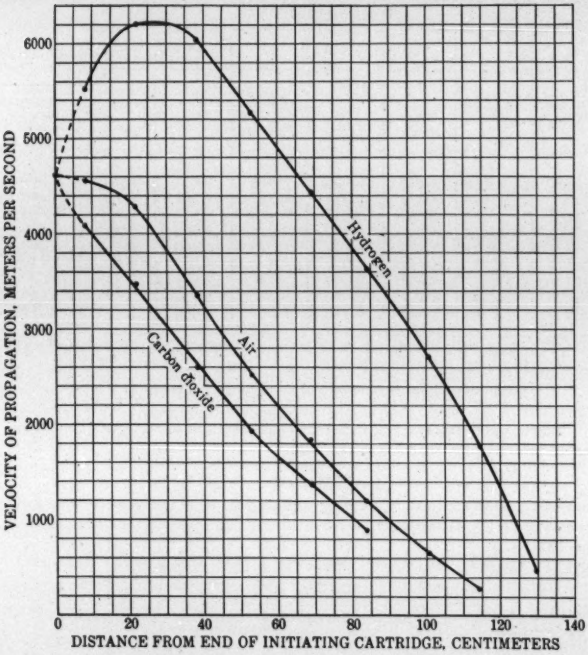
[c] Reciprocal of column 7 × increase in gap length in meters gives the instantaneous velocity over that length in m./sec.

TABLE 4.

Calculated "Instantaneous" Velocity of Propagation of Disturbance in Gas-gaps.

Distance of Mid-point from End of Initiating Cartridge, Cm.	7.6	22.9	38.1	53.4	68.6	83.8	99.1	114.3	129.5
Velocity of propagation m./sec.									
Explosive No. 10									
Hydrogen	5,560	6,200	6,050	5,240	4,420	3,610	2,720	1,770	470
Air	4,570	4,270	3,350	2,520	1,870	1,200	632	260	
Carbon dioxide	4,060	3,430	2,600	1,920	1,370	900			
Explosive No. 11									
Hydrogen	3,990	4,970	3,500	2,510	1,580	710			
Air	3,520	2,740	1,820	1,240	710				
Carbon dioxide	3,020	2,160	1,450	950					
Explosive No. 12									
Hydrogen	3,110	3,630	3,910	3,540	2,910	1,890	445		
Air	2,700	2,740	1,900	1,340	830	420			
Carbon dioxide	2,530	1,880	1,230	520					

Fig. 2.



Velocity of propagation of disturbance initiated by explosive 10 in a gas gap.

Table 5.

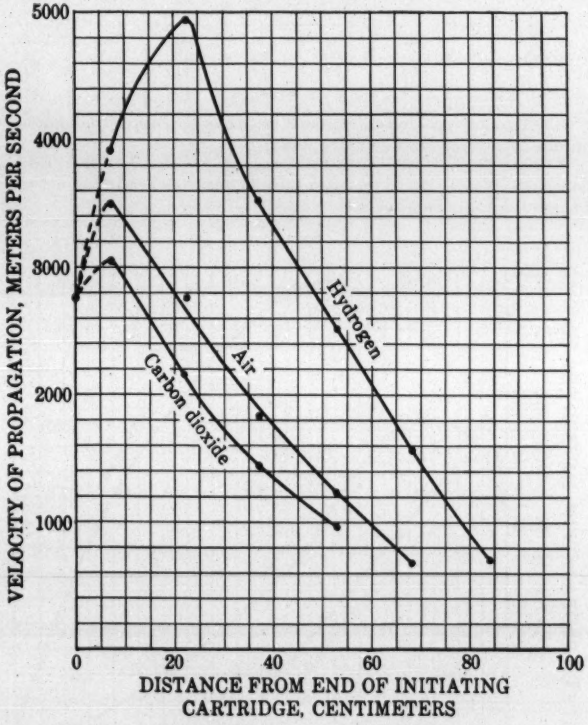
Velocity in Air-gap when Cartridges[a] Are Confined in Shelby Steel Tubing.

Distance measured (explosive plus gap),	30.5	45.7	61.0	76.2	106.7	137.0	198.2	259.0	442.2	558.8
Length of gap, cm	15.25	30.5	45.7	61.0	91.5	121.9	183.0	243.8	427.0	543.6
Rate of explosive and gap, m./sec. measured	2,970	3,280	3,180	3,260	3,270	3,280	3,380	3,260	2,920	2,650
From smoothed curve	3,200	3,190	3,230	3,260	3,300	3,320	3,330	3,300	2,920	2,650
Instantaneous velocity, m./sec	2,820	3,180	3,340	3,390	3,400	3,380	3,370	3,200	2,520	1,960

[a] First cartridge explosive 13, second cartridge explosive 14.

gaps of air, hydrogen, and carbon dioxide. Table 5 and Fig. 5 show the results obtained when the cartridges were confined in steel tubes. Table 6 gives the distances over

FIG. 3.



Velocity of propagation of disturbance initiated by explosive 11 in a gas gap.

which detonation will propagate from one cartridge to another over a gap in paper tubes containing either hydrogen, air, or carbon dioxide.

Table 6.

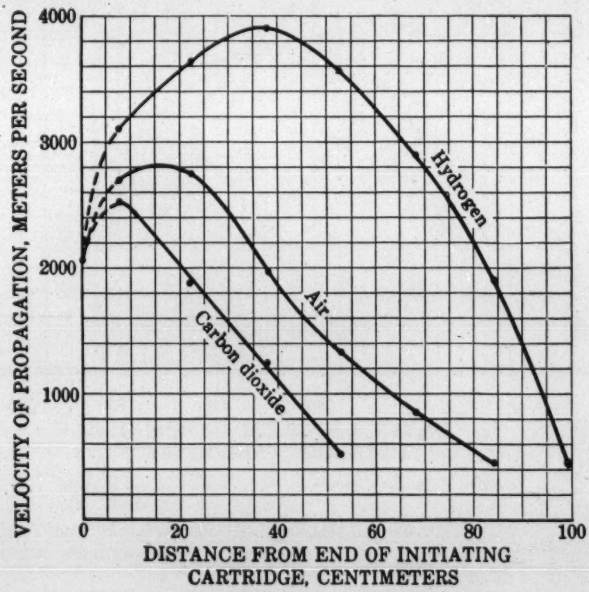
Distance over Which Detonation is Propagated in Paper Tubes.
A. Initiator and receiver of same explosive.

Explosive No.	10		11		12	
	Explosion [a]	No explosion [b]	Explosion	No explosion	Explosion	No explosion
	cm.	cm.	cm.	cm.	cm.	cm.
Hydrogen	137	203	25	38	23	38
Air	107	178	51	64	30	51
Carbon dioxide	61	122	30	46	25	46

[a] "Explosion" indicates the maximum distance over which detonation always propagated from one cartridge to the other.

[b] "No explosion" is the minimum distance over which detonation did not propagate in four trials. In the range between, the second cartridge sometimes detonated and sometimes did not.

Fig. 4.

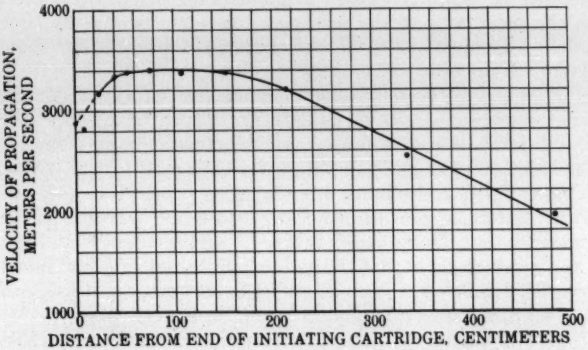


Velocity of propagation of disturbance initiated by explosive 12 in a gas gap.

B. Initiator as indicated and receiver 40 per cent. straight dynamite.

Explosive No.	Maximum distance over which detonation always propagates, cm.		
	10	11	12
Hydrogen	137	107	76
Air	107	76	61
Carbon dioxide	61	61	46

FIG. 5.



Velocity of propagation of disturbance initiated by explosive 13 in Shelby steel tubing.

CONCLUSIONS.

The following conclusions may be drawn from a study of the data:

1. The time taken for detonation to be transmitted across a gap between two cartridges of explosive in a paper tube is a function of the length of the gap and (*a*) the nature of the gas in the gap, (*b*) the rate of detonation of the initiating charge of explosive, and (*c*) the sensitivity of the receiving charge of explosive. Under these headings the data indicate that—

(*a*) The velocity is most rapid in gases of low density such as hydrogen or helium, and slowest in heavy gases such as carbon dioxide.

(*b*) With hydrogen in the gap, the initial velocity of the disturbance in the gap is always greater than the rate of

detonation of the explosive and increases over the first 30 cm. of the gap. In air and carbon dioxide this effect occurs only with the slower explosives, which are those having rates of detonation below 3,000 m. per second.

(*c*) As the length of gap is increased, speeds determined by the Mettegang recorder begin to be erratic. Photographs of the phenomenon show a distinct and variable lag between the instant at which the second cartridge is struck by the first disturbance and the instant at which it detonates. The distance at which this effect begins to take place will depend on the sensitivity of the receiving cartridge, hence, the time taken for transmission of detonation will depend to some extent on the sensitivity of the receiving cartridge.

2. When the system is confined in a steel tube of about the same diameter as the cartridges, the length of air-gap over which detonation will propagate is increased more than 10-fold; for example, the gap length for explosive 13 was 0.8 m. in paper tubes and 9 m. in a Shelby steel tube. The velocity of the disturbance in the steel tube does not decrease at the same rate as it does in paper tubes. This is evident from Figs. 3 and 5, which show that the instantaneous velocity had fallen to a value of 2,000 m. per second in an air-gap at a distance of 0.35 m. in a paper tube and at 4.6 m. in a steel tube.[10]

3. The maximum distance over which detonation is transmitted varies with the character of the initiating and receiving charge of explosive and the nature of the gas in the gap.

Discussion of Findings.

The relative speeds of the disturbance in hydrogen, air, and carbon dioxide are of the order to be expected if this disturbance is a discontinuous wave phenomenon of high intensity. Furthermore, the long length of air-gap over which detonation of the second cartridge takes place in steel tubes and the maintained high speed of the disturbance would also seem to indicate transfer by wave motion of this type—that is, a shock wave. However, there is some indication that as the length of gap is increased to a certain point, the second cartridge does not always detonate when struck by the wave, but it may detonate later. Results become erratic after the gap

[10] Explosives 11 and 13 used in paper and steel tubes respectively were different lots of the same type of explosive.

has reached a length of 20 to 40 cm. less than the gap length at which propagation fails completely. These results have been included in the calculations on which Figs. 2, 3, and 4 are based and give rise to calculated velocities less than that of sound over the last part of the longest gaps. This would indicate that the second cartridge did not detonate when struck by the shock wave but was set off by a later disturbance, perhaps by the gaseous products of explosion. This would give rise to the apparently very low velocities over the latter part of the gap. Photographic evidence that such a lag exists is introduced later.

From the data presented, it seems probable that there is a critical velocity of the shock wave (peculiar to each explosive) for speeds above which the shock wave itself initiates immediate detonation in the receiving cartridge and below which it does not have this effect. The largest gap then should be obtained for the most sensitive receiver and for a medium in which the shock wave has, and maintains, a high speed of propagation. With an insensitive receiver, we should expect the distance of propagation to be independent of the nature of the gas in the gap.

In this connection, figures for maximum distances over which detonation is propagated (Table 6, *A* and *B*) are of interest. The data in Table 6, *B*, show that when the receiving cartridge is the sensitive explosive No. 10, the maximum distance of propagation is always highest with hydrogen in the gap and lowest with carbon dioxide, whatever explosive is used as initiator. When both receiver and initiator are of the same explosive, the maximum gap is much lower with the less sensitive explosives Nos. 11 and 12, and is somewhat higher with air than with carbon dioxide or hydrogen. The explanation of this difference is evidently connected with the sensitivity of the receiving cartridge. Reaction of the gaseous products with air may account for the longer distance of propagation when air is employed in the gap.[11]

[11] Later experiments with another permissible explosive indicate that when the gap contains air or oxygen, reaction of the gaseous products of explosion with oxygen increases the distance over which detonation is propagated. Maximum gap lengths over which detonation always propagated were as follows: N_2, 10 cm.; air, 15 cm.; O_2, 23 cm.; H_2, 8 cm.; CO_2, 8 cm.

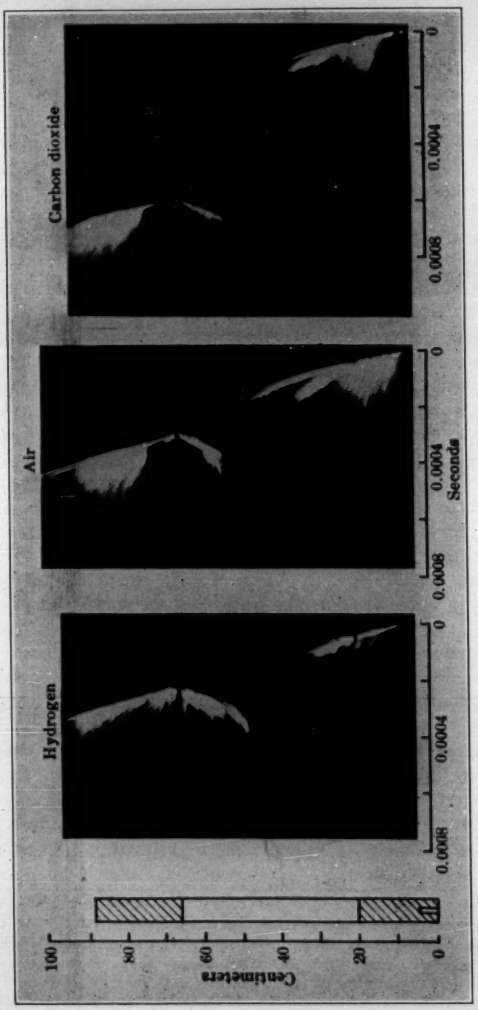


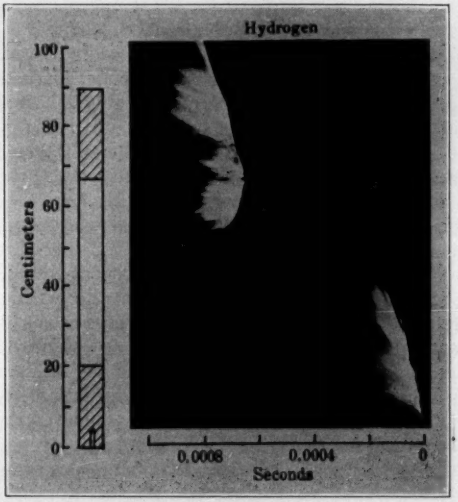
Fig. 6.

Photographs showing effect of different gases in gap.

PHOTOGRAPHIC ANALYSIS.

The photographic method previously described[12] was employed to check the results obtained with the Mettegang recorder. The method was modified according to the technique recently described by Jones.[13] The explosive is placed behind a horizontal slot 0.1 cm. in width cut in a sheet of armor plate 2.5 cm. in thickness. This method gives much

FIG. 7.



Example of delayed detonation of second cartridge of explosive.

sharper definition than when a slit is placed in front of the film. The three photographs shown in Fig. 6 are of two cartridges of explosive No. 11 separated by a 45-cm. gap of hydrogen, air, and carbon dioxide, respectively. The cart-

[12] Perrott, G. St. J., and Gawthrop, D. B., "Photographic Measurement of Rate of Detonation of Explosives," J. FRANK. INST., Vol. 203, 1927, pp. 103–110.

[13] Jones, E., "Photographic Study of Detonation in Solid Explosives," Part I, *Proc. Roy. Soc.*, A., Vol. 120, 1928, pp. 603–620.

ridges were wrapped in cellophane tubes. The second cartridge was primed with a 2-cm. slice of 40 per cent. straight dynamite to make sure that detonation took place. The results show graphically the difference in speed of propagation in the three gases. Two flames are evident just above the initiating cartridge—the faster one is in the cellophane tube and the other is the flame from the expanding products outside the tube. Velocities obtained by the photographic method check those obtained with the Mettegang recorder.

Fig. 7 shows an example of the delay or lag on detonation referred to previously. On the original negative it is possible to see a faint luminous disturbance proceeding from the initiating cartridge at a rapid rate up the tube, hitting the end of the second cartridge, and there producing a luminous dot. The cartridge does not detonate, however, until 0.5 millisecond later. These delayed ignitions occur when the gap between cartridges is getting near the limit beyond which propagation ceases to take place. Because the Mettegang recorder measures only the total time between detonation of the two cartridges, these lags may show up in the calculated results as speeds of propagation less than the velocity of sound. Actually, it seems to be evident that the second cartridge is not being detonated by the shock wave in the case of the long gaps, but is caused to detonate by the expanding gaseous products.

A forthcoming paper will discuss the mechanism of this process more fully and will describe an investigation by the Schlieren method in which pressure-wave photography has been employed in analyzing the mechanism of transfer of detonation across a gap between two cartridges of explosive.

ACKNOWLEDGMENT.

Our best thanks are due W. C. F. Shepherd, of the Safety in Mines Research Board of Great Britain, for advice and criticism during the preparation of this paper, and to N. A. Tolch, Assistant Mining Engineer, who made the measurements in steel.

Explosives Section,
August 12, 1929.

THE LATENT IMAGE. A CRITICISM.

BY

HENRY LEFFMANN,

Life Member (Honary) of the Institute.

"LATENT Image" is a term of photography indicating the invisible effect of the action of light on a sensitive emulsion. Strictly speaking, the invisibility is relative, for after long exposure some traces of the effect of the brighter portion (high lights) of the picture can be seen. This relative latency applies to silver bromide and iodide. Silver chloride shows promptly the influence of light. It was, indeed, by this property of silver chloride that the clue to photographic procedure was obtained. In 1727, Heinrich Schulze showed by a simple experiment that the darkening of a silver compound was due to light, not to heat or air as had been theretofore supposed.

With the modern dry-plate, the latent image remains for a long while, but not indefinitely. It can be at once rendered visible by a simple process, known as development, which consists in reducing to the metallic condition some of the silver of the halides in the emulsion. A large number of substances ranging from ferrous compounds to complex organic derivatives are available for the purpose, all more or less active reducing agents. In this action, the reduced silver deposits on the parts which have been impressed by light, and thus the latent image becomes visible, but is reversed in form, since the parts of the object that were brightest are represented by an opaque deposit of silver and the darkest parts by unchanged halide. In the ordinary procedure, the plate is immersed in a solution of sodium thiosulphate (hypo) by which the unchanged halide is completely dissolved and therefore the darkest parts of the object are represented by clear glass, constituting the "negative."

The nature of the latent image has been the subject of much research and discussion. A large volume of literature

is now available, but no positive decision has been attained, at least nothing universally accepted. It has been proved that a small amount of the halogen is set free, but whether this is due to the complete decomposition of some molecules, leaving free silver, or to partial decomposition, by which a sub-halide is formed is not known. The experimental data, showing the escape of the halogen, are explicable on either theory.

The recent investigators of the problem seem to have made their studies within a narrow field. Several peculiar phenomena have been ignored, all of which seem to be unexplained by the theories that have been proposed. The first of these is the possibility of "developing after fixing," that is removing entirely the silver compounds and obtaining by a special development the picture in every detail. So far as can be judged by careful inspection of the plate no halide is left. It seems, therefore, that the latent image is in the material in which the halide was suspended, gelatin almost always now-a-days, but similar results can be obtained with the collodion plates in what is known as the "wet process." So far as I am aware no writer on the nature of the latent image has attempted to deal with this phenomenon or to account for it on the theory that he sets forth.

Another but equally peculiar phenomenon is that when a plate is very much over-exposed, the lighting is reversed, that is, the developed and fixed plate is a positive. This not infrequently happens in taking photographs of lightning, from the intense actinic power of the spark. The effect, however, of very great excess of exposure has another remarkable feature. It was investigated in considerable detail by Professor Nipher of Washington University, St. Louis, Missouri. Using rapid plates he prolonged exposure for several hours, so that he obtained well-marked positives but he found that if such plates are developed in the dark room, more or less fog will be produced. Nipher's results were confirmed by members of the Photographic Section of the Franklin Institute. A plate that had been given several hours exposure, was developed in a tray in front of a sixteen candle power (white) bulb. When fixed it showed a perfect positive with no trace of fog. Another plate that had been

given a long exposure and then developed in the dark room was shown. It had considerable fog.

A third class of phenomena also requires consideration. Emanations at ordinary temperatures from some of the more volatile metals (Al, Zn, Hg, Mg) will produce effects on the dry plates which may be brought out by the usual methods of development. These impressions will also remain if the plate is first fixed and then developed. What is the nature of the latent image in these cases?

Development after fixing, the curious phenomena observed as result of great over-exposure, and the effects of exposure of plates to the emanations of metals at ordinary temperatures (not radio-activity) seem not to be explained on the theories now generally advocated concerning the nature of the latent image. The manner in which these peculiar phenomena are ignored in the discussions on the subject is puzzling.

A Dynamical Method for the Determination of Young's Modulus by Bending. KAMTA PROSAD. (*Phil. Mag.*, March, 1929.) Usually a static method is employed for the determination of Young's modulus. The extension of a vertical wire is measured under the successive addition of increasing weights or, by 'sGravesande's method with a horizontal wire, the sinking of its middle point under growing load is observed, in the case of a bar a flexure method is often used. The author presents a method whereby the modulus is found by measurements made while a bar is in lateral vibration. The theory of the vibration of bars vibrating laterally with one end fixed shows that, as the length of the bar is changed, the square of the frequency of vibration is equal to the reciprocal of the fourth power of the length of the vibrating portion multiplied by a factor that is constant for a given bar and is dependent on its thickness, its Young's modulus and its density and on nothing else so long as the type of vibration does not change. A bar of metal was made to vibrate laterally by electrical means and its frequency was determined as the length of the vibrating part was varied step by step. Then the square of the frequency was plotted against the reciprocal above defined. The resulting curve is a straight line from which the factor of proportionality is obtainable. This furnishes Young's modulus since all the other quantities entering into it are easily found.

The frequency was got by having a stylus attached to the bar record upon a smoked cylinder. When the material of the bar was non-magnetic, a thin sheet of soft iron was attached to the free end of the bar so that an electromagnet might maintain the state of vibration. Correction was made for the stylus and iron sheet which had the effect of lengthening the vibrating part of the bar. A comparison of results obtained by this method with those from flexure are given in the following table:

	By Prosad's method dynes/sq. cm.	Flexure method dynes/sq. cm.	From Kaye and Laby's Tables, dynes/sq. cm.
Steel.....	19.49×10^{11}	20.26×10^{11}	19.5 to 20.6×10^{11}
Brass.....	9.29 " "	9.79 " "	9.7 to 10.2 " "
Glass.....	7.56 " "	6.38 " "	6.5 to 7.8 " "

G. F. S.

NOTES FROM U. S. BUREAU OF STANDARDS *

CEMENT REFERENCE LABORATORY.

THE cement reference laboratory, established during the last fiscal year as a coöperative effort of Committee C-1 on Cement of the American Society for Testing Materials and the Bureau of Standards, to promote uniformity and improvement in cement testing, has been engaged for several months in field inspection of cement laboratories. The inspectors may not visit some localities for considerable periods of time, and on that account the following tolerances on apparatus should be of interest to those laboratories which desire to examine and adjust their apparatus or write purchase specifications for new apparatus. It should be understood that these tolerances are "proposed tolerances," and have not at this time any official standing as accepted standards or tentative standards of the American Society for Testing Materials. However, the cement reference laboratory is operating under these tolerances.

PROPOSED REVISIONS IN A. S. T. M. STANDARD SPECIFICATION C 9-26

PROPOSED TOLERANCES ON APPARATUS.

1. Insert at the end of Section 35 the following:

"The Vicat apparatus shall meet the following requirements:

Weight of plunger	300 g. (0.661 lb.) ± 0.5 g. (8 grains)
Diameter of larger end of plunger	1 cm. (0.394 in.) ± 0.02 mm. (0.001 in.)
Diameter of needle	1 mm. (0.039 in.) ± 0.01 mm. (0.0005 in.)
Inside diameter of ring at bottom	7 cm. (2.75 in.) ± 3 mm. (0.12 in.)
Inside diameter of ring at top	6 cm. (2.36 in.) ± 3 mm. (0.12 in.)
Height of ring	4 cm. (1.57 in.) ± 0.5 mm. (0.02 in.)."

2. Insert at the end of Section 45 the following:

"The Gillmore needles shall meet the following requirements:

* Communicated by the Director.

Initial needle

Weight 1/4 lb. (113.4 g.) ± 8 grains (0.5 g.)

Diameter 1/2 in. (2.11 mm.) ± 0.001 in. (0.02 mm.)

Final needle

Weight 1 lb. (453.6 g.) ± 8 grams (0.5 g.)

Diameter 1/24 in. (1.06 mm.) ± 0.001 in. (0.02 mm.)."

3. Replace sub-note (3) of Section 31, Note 1, with the following:

"The balance used in making the fineness test shall meet the following requirements: The balance shall be enclosed in a glass case. On balances in use the tolerance to be allowed at a load of 50 g. shall be ± 0.05 g., and at loads less than 0.1 g. the tolerance shall be ± 0.01 g. (The tolerance to be allowed on new balances shall be one-half of the value given.) The maximum sensibility reciprocal allowable at each of the loads specified above shall be twice the value of the tolerance specified for the load in question. The sensibility reciprocal is a measure of the sensitivity of a balance, and is the weight required to move the position of equilibrium of the beam, pan, pointer, or other indicating device of a scale a definite amount at the capacity or at any lesser load. For a complete definition of sensibility reciprocal see Bureau of Standards handbook M 85, pp. 80–82."

After sub-note (5) insert an additional sub-note, as follows:

"6. The tolerances to be allowed in excess or deficiency on the weights in use in the fineness test shall be as follows:

Weight.	Tolerance.	Weight.	Tolerance.
50 g.	0.04 g.	0.500 g.	0.003 g.
20	.02	.200	.002
10	.014	.100	.001
5	.010	.050	.001
2	.006	.020	.001
1	.004	.010	.001

The tolerances to be allowed on new weights shall be one-half the values given."

4. Add to Section 33 a note to read as follows:

"The scales used in weighing materials for neat cement

and mortar mixes shall meet the following requirements: On scales in use the tolerance to be allowed at a load of 1000 g. shall be ± 1.0 g. (The tolerance to be allowed on new scales shall be one-half of the values given.) The sensibility reciprocal (see Note 1 (3) under Determination of Fineness) shall be not greater than twice the tolerance.

"The tolerances to be allowed in excess or deficiency on the weights in use in weighing materials for neat cement and mortar mixes shall be as follows

Weight.	Tolerance.	Weight.	Tolerance.
1000 g.	0.5 g.	20 g.	0.05 g.
500	.35	10	.04
200	.20	5	.03
100	.15	2	.02
50	.10	1	.01

"The tolerances to be allowed on new weights shall be one-half the values given."

5. Add to Section 33 a note to read as follows:

"Glass graduates of 100 ml. to 200 ml. capacities used for measuring the mixing water shall be made to deliver the indicated volume at 20° C. (68° F.). The tolerance to be allowed on these graduates shall be ± 1.0 ml."

6. Insert at the end of Section 47 the following:

"The dimensions of the briquette molds shall meet the following requirements: width of mold, between inside faces, at waist line of briquette, 1 in. ± 0.01 in.; thickness of mold 1 in. ± 0.004 in. The tolerances to be allowed on new molds shall be one-half the values given."

7. Amend Section 52 as follows:

In place of portion commencing in line 3 with "The machine shall be capable . . ." and ending in line 8 with ". . . any lesser load," insert the following:

"The error for loads of not less than 100 pounds shall not exceed ± 1.0 per cent. for new machines or ± 1.5 per cent. for used machines."

Also add to the last sentence of this same paragraph "± 25 pounds per minute."

8. Insert at the end of Section 55 the following:

"The relative humidity of the moist closet shall not be less than 90 per cent."

9. Add the following note after Section 28:

"*Note:* The balances used in the chemical analysis shall meet the following requirements: capacity not less than 100 grams in each pan; the two arms of beam to be equal to within one part in 100,000; capable of reproducing results within 0.1 mg.; sensibility reciprocal (see note under Determination of Fineness) not more than 0.2 mg. per division of the graduated scale. The weights used in the chemical analysis shall conform to the requirements of the Bureau of Standards specifications for Class 'S' weights as contained in Bureau of Standards Circular 3."

PRESERVATIVE TREATMENTS FOR STONE.

ALTHOUGH preservative treatments for stone have been used for a considerable period of time, their value has often been questioned. The type of preservative most frequently used in this country consists of a wax or stearate dissolved in a volatile solvent which is applied to the masonry with a spray or brush. This solution penetrates the pores of the masonry, and as the solvent evaporates the wax is left in the pores forming a more or less effective seal. The preservative effect is supposed to be gained by preventing a penetration of moisture, thus overcoming the action of frost or other harmful effects which may result from dampness inside the masonry.

It has been proved that such treatments do not entirely seal the surface pores of stone and for this reason there has been considerable doubt concerning their value, especially where the stone is subjected to abnormal amounts of dampness. The theory is sometimes advanced that, to seal or partially seal the surface pores when water can penetrate through or behind the treatment will cause a condition under which the stone will decay from frost action at a more rapid rate than if the surface pores were left open. Since frost action on stone is the result of expansion of water in passing from the liquid to the solid state, this theory seems to be entirely sound for masonry exposed to very damp conditions

where the material can become highly saturated; because the treatment would seem to hinder or prevent the extrusion of ice through the surface pores, and hence higher internal stresses would develop than if there were no surface seal.

In order to test this theory some experiments have recently been made at this bureau on parallel series of stone specimens, one of which was treated with a 10 per cent. solution of paraffin in benzol and the other left in the original state. Two sandstones and two limestones were selected for the experiments, all of which were known to have rather low resistance to frost action. After treating half the specimens of each kind with the preservative, the two series were soaked in water for 14 days and absorption tests made during this time after periods of 30 minutes, 24 hours, and 14 days. While all of the treatments were indicated to be effective to the extent of greatly reducing the rate of absorption, at the end of the 14-day period the treated specimens had absorbed from 68 to 95 per cent. as much as the untreated specimens. The two series were then placed in ½-inch of water in a tray and placed in the freezing chamber until frozen, after which they were taken out and thawed in water at room temperatures. This cycle was repeated until the specimens were all disintegrated.

In these experiments all of the treated specimens showed higher resistance to frost than the untreated ones. The increased resistances computed as a percentage of the number of freezings required to disintegrate the treated material were as follows: One sandstone was improved 350 per cent., another 260 per cent.; one limestone was improved 190 per cent., and the other 53 per cent.

These experiments indicate that such a preservative treatment is of value on the types of stone under consideration even under very severe conditions of soaking. It also seems probable that where such stones are placed in the walls of a building and exposed only to the intermittent soaking of rains or thawing snow that the treatments would be far more effective than indicated by these experiments.

SAGGER INVESTIGATION.

THE most recent reference to this investigation was made in *Technical News Bulletin*, No. 142 (February, 1929), in which were reported the results of a preliminary study of a series of sagger bodies using varying combinations of clays and grogs. Among the results obtained it was found that the porosity of the fired sagger body bears a very important relation to the resistance of saggers prepared from it to failure from heat shock. In order, therefore, to determine the range in porosity most effective toward prolonging sagger life, a systematic study has been undertaken of a series of sagger bodies which have been fired at different temperatures so as to give a range in values for this property. With this work is also included a more extended study of the effect of using in a body a close burning clay as grog in comparison with grog made from an open burning clay.

A total of 38 different bodies have been prepared from clays and grogs of known properties and 300 small oval saggers and 425 specimen bars made from them. Five saggers and six specimen bars each of 14 different bodies were fired at three temperatures ranging from approximately 1,190 to 1,270° C. (cones 8, 10, and 12). Saggers and bars prepared from the remaining bodies were fired at either or both 1,230 and 1,270° C. The results of the test for determining the resistance of saggers to thermal shock gave the lowest temperature of failure of any one set of saggers at 350° C. and the highest temperature at 890° C. The majority of saggers had failed at or below 575° C. It would appear that those sagger bodies which had not failed at or below 600° C., a critical temperature possibly due to quartz inversion, might be expected to resist failure on being quenched from considerably higher temperatures.

Determinations are being made at present of the plastic flow of the fired bodies under load at 1,000° C. A rather unexpected result was obtained when it was found that the plastic flow of the body decreased with increased temperature of firing. The relation is not proportional, but the order of values is quite definite.

ABSOLUTE MEASUREMENT OF GAGE BLOCKS BY INTERFEROMETER.

The Zeiss interference comparator has been extensively used during the month to check a number of the bureau's master precision gage blocks. Certain difficulties experienced with this instrument when received from the manufacturers have been largely overcome. The rise in temperature in the chamber containing the gage blocks resulting from conduction of heat from the helium lamp which was supported on the instrument itself was eliminated by removing the lamp a distance of seven inches from the slit and using a small lens to focus an image of the lamp on the slit. It was planned to provide the extension tube now supporting the lamp with ventilating holes, but this has not seemed necessary as no perceptible rise in temperature has been noticed in the gage block chamber during the time required to make a determination of the length of a gage block.

When the instrument was first used it was noticed that there was an apparent difference in wave-length from one edge to the other of the colored bands, produced by the lines in the helium spectrum. This appears to be true both with lines supposed to be single and those known to be doublets. The center of the colored bands is now being used in all cases. In most cases, where the lengths previously measured by the bureau's interferometry section have been remeasured by the Zeiss comparator in the gage section, values have been checked within 0.000002 inch and frequently within 0.000001 inch. In a few cases the bureau's masters are changing, as values obtained several months apart indicate continuous change in the same direction. These changes make the ready availability of means for absolute measurement of considerable importance.

To all absolute readings obtained with the interferometer, a correction must be applied depending on the density of the air. One source of error in determining this correction has been found to lie in the fact that in a room where the temperature frequently varies several degrees in short intervals, the thermometer on a barometer does not indicate accurately the temperature of the mercury or of the barometer scale. This uncertainty has caused errors as great as 0.0000015 in

the air density correction for a one inch block. The bureau plans to move the barometer from the main gage section room to the constant temperature room to reduce this uncertainty. The makers of the Zeiss instrument recommend a phase change correction of 0.0000016 inch for gage blocks, but experiments have shown this correction to be too small for precision gage blocks of American make. The bureau is now using a phase change correction of 0.0000025 inch which is the value used by the interferometry section. With the Zeiss instrument, using helium, blocks up to one inch can be measured; the limit on length with the Pulfrich is less than this. Krypton tubes recently purchased permit measurements up to two inches; however, the tubes are not entirely satisfactory as it was expected that a length of at least six inches could be measured.

MEETINGS OF NATIONAL SCREW THREAD COMMISSION AND AMERICAN GAGE DESIGN COMMITTEE.

MEETINGS of the National Screw Thread Commission and the American Gage Design Committee were held at Greenfield, Mass., on September 9 and 10. The National Screw Thread Commission met on September ninth and considered the following items:

1. Discussion of proposed revision of certain bolt head and nut dimensions.
2. Tolerances on bolt and screw stock.
3. Screw threads for gas cylinder valves.
4. Screw threads for acid drums.
5. Specifications for reversible gage blanks.
6. Washer screws for water faucets.
7. Discussion of gage classification.
8. Status of report on slotted head products.
9. Checking three-flute and five-flute taps, and inspection of dies.
10. Specifications for material or quality of bolts.
11. Consideration of abridged reports.
12. Discussion of use of non-standard threads by automobile manufacturers.
13. Correspondence regarding revision of S. A. E. Handbook.

14. Thread locking devices.
15. Socket-head cap and set screws.
16. Relative advantages of coarse and fine pitch threads.
17. Discussion of chart for determining helix angle of threads of various diameters and pitches.
18. Government specifications for hose coupling threads.
19. Relative value of various classes of fit.
20. Preliminary discussion of methods of gaging taper threads.
21. Appointment of delegates to World Engineering Congress, Tokio.

Under item 1 it was voted to make certain changes in the 5/8 inch bolt-head and nut dimensions to bring them into conformity with the recommendations of the Bolt, Nut, and Rivet Manufacturers' Association as approved by the sectional committee on bolt, nut, and rivet proportions.

The question of increasing the tolerance on major diameter of certain sizes and classes of screws and bolts was discussed under item 2. The evidence presented seemed to show that there is no necessity for such increase, since manufacturers are able to buy hot rolled stock within present tolerances without extra cost, if they so specify in their orders. This applies to classes 1 and 2 in sizes where hot rolled stock is commonly used. Under item 3, Navy specifications for gas cylinder valves were presented for discussion, and a special committee was appointed to give the matter further study. Screw-threads for acid drums (item 4) were also referred to the same committee.

After considering item 5, the commission approved the recommendations of the American Gage Design Committee covering gage blanks for reversible plug gages. Specifications for these blanks had not been completed at the time the remainder of the work of the American Gage Design Committee was approved by the commission.

Under item 6, a special committee was appointed to take up the matter of standardizing the washer screws used in water faucets. A collection of the screws now in use for this purpose was exhibited.

A discussion of the gage classification as contained in the 1928 report took place under item 7. It has been held by

some that only class X gages are required by industry; the commission, however, believes that there is a need for class Y and Z gages, and took no action toward changing from the present classification.

Under item 8, the status of the report of the sectional committee subcommittee on slotted head products was discussed. This report has not yet been finally approved by the sectional committee.

Under item 9, a brief description was given of the methods used by the Bureau of Standards in checking three- and five-fluted taps.

After considering item 10, the commission reaffirmed its attitude that the commission is not concerned with material, but only with dimensions of threaded products.

Under item 11, it was stated that three sections of the 1928 report are being published as separate reports for shop use. These abridged reports are as follows: (*a*) regular coarse and fine thread series; (*b*) threads of special diameters, pitches, and lengths of engagement; and (*c*) design of blanks for plain and thread plug and ring gages from .059 inch to 4.510 inches in diameter.

The discussion under item 12 brought out the opinion that while there is still considerable use of non-standard threads in automobile work, most of this is confined to old designs and replacements, and that practically all new work is strictly in accord with the American National Screw Thread Standards.

It was agreed that the commission will take up with the Society of Automotive Engineers Screw Thread Committee at its next meeting the 12 pitch series and the extension of the fine thread series as contained in the 1928 report (item 13).

The consideration of item 14 brought forth the statement that while the commission has not gone into the question of thread locking devices, a comprehensive investigation is now being carried out at the Bureau of Standards to determine the relative value of such devices. This investigation is being supported by manufacturers of threaded products.

Under item 15 it was reported that a subcommittee of the sectional committee on bolt, nut, and rivet proportions is working on this subject. The commission took no action.

The importance of correct helix angle in screw threads was discussed (items 16 and 17), and a chart was presented from which designers and others can readily obtain the helix angle of any thread of known diameter and pitch. The fact was mentioned that it has been found to be good engineering practice to use the so-called "fine" threads in the smaller sizes and the "coarse" threads in the larger sizes. The reason for this apparently is that the smaller sizes in the fine thread series have practically the same helix angle as the larger sizes in the coarse thread series. They are, therefore, of about the same "fineness." Two of the members were of the opinion that a single consistent series having a helix angle of approximately 2 or 3 degrees would be found adequate and satisfactory for most holding purposes.

Under item 18, the secretary reported that a sectional committee is now considering the further standardization of hose threads, other than fire-hose threads, and that it will be advisable for the commission to coöperate with this committee. A copy of the Federal specifications for hose threads was also presented.

Upon taking up item 19, there was an informal discussion of the question of the relative advantages of the various classes of fit, and the fact was brought out that there are very few reliable data available as to the relative strength of the various classes of fit, the effect of lead error, or as to the relative tendency of the various classes to work loose in service. It was recommended that an extensive research be carried out in this important field.

Under item 20, a preliminary discussion was presented of a proposed method of gaging taper threads. The proposed method, if put into effect, will result in a simplification of gages. It will establish definite high and low limits for the product, in place of the present method of allowing $1\frac{1}{2}$ turns either way from an ideal size which can not readily be measured.

After considering the last item, No. 21, the commission appointed Dr. George K. Burgess, Colonel J. O. Johnson, and Mr. L. D. Burlingame as its official delegates to the World Engineering Congress, Tokio, Japan.

Following the meeting of the Screw Thread Commission

the Technical Subcommittee and the Editorial Subcommittee of the American Gage Design Committee held a series of meetings for the purpose of reading the galley proof of the report of the Committee which is being printed as Miscellaneous Publication No. 100, Bureau of Standards.

The committee will meet in January, 1930, to consider extending the work of gage standardization to other types of limit gages.

PAPER CELLULOSE DETERMINATIONS.

A NUMBER of alpha-cellulose determinations have been made on various kinds of paper, to compare the method in use at the bureau with that proposed by the American Chemical Society. These indicate that the American Chemical Society method for cellulose materials cannot be applied satisfactorily to paper without modification of the form of the sample and the method of filtering it. Owing to the resistance paper offers to disintegration into its component fibers, it was found necessary to grind the test specimen to a cotton-like form, as when the specimens are simply cut into small pieces as specified in the American Chemical Society method, the extractions are not complete.

For filtration of the finely-ground material, the use of cloth in a Buchner funnel was found necessary, instead of using a Gooch crucible as described in the American Chemical Society method. Otherwise, the two methods give test results that are in good agreement. The Bureau of Standards method is the less time-consuming.

Further study of the copper-number determination indicates that a modification proposed by Braidy gives increased accuracy. He replaces the Fehling solution with a solution of copper sulphate made alkaline with sodium bicarbonate and sodium carbonate, and heats for three hours in a bath having a temperature of 100° C. By means of this modification of the bureau method, the average deviation of individual results from the mean, in the case of fourteen samples tested, was reduced to one per cent. Without the modification the deviation was six per cent.

STANDARD METHOD FOR THE DETERMINATION OF WEIGHTING ON SILK.

The following method for the determination of weighting on silk has been worked out with the coöperation of a number of commercial laboratories. It has been approved as a standard method by the Joint Technical Committee on Silk Weighting. This committee has recommended its adoption by the Joint Committee on Weighting, which includes such organizations as The Silk Association of America, The National Retail Dry Goods Association, The Better Business Bureau, etc.

I. *General.*—1. By "weighting" is meant not only metallic weighting, but all materials other than fibroin present in the finished silk after it has been dried to constant weight in air at 110° C.

2. The amount of weighting is expressed in per cent. of the weight of the finished silk after it has been dried, as above.

II. *Sampling.*—A sample taken for analysis should be representative of the material. It is recommended that a strip measuring from two to four inches wide be taken all the way across the original cloth from selvage to selvage. The sample should weigh from 1 to 5 grams.

III. *Test for Silicate.*—A small sample of the silk is ignited, the ash is placed in a platinum crucible and two drops of concentrated hydrofluoric acid are added. If silicate is present, chemical action accompanied by a considerable amount of heat will be noticed.

IV. *Tin Phosphate Silicate Weighted Silk.*—1. The sample is dried to constant weight in an air oven at 100° C. This is called weight A.

2. The dried sample is soaked in 100 times its weight of distilled water at 65° C. for 20 minutes. It is moved about in the water every few minutes during this time in order to insure thorough penetration of water and extraction of water-soluble materials. It is then rinsed in a fresh portion of distilled water, then in alcohol, and finally in ether, after which it is dried to constant weight, as above. (Two 25 cc. portions of alcohol and of ether are usually sufficient.) This is called weight B.

$$\text{Weight A} - \text{Weight B} \times 100/\text{Weight A} = \text{Finishing materials in per cent.}$$

3. The sample from which "finishing material" has been removed is soaked in 100 times its weight of 2 per cent. hydrofluoric acid solution at 65° C. for 20 minutes. It is then rinsed in water and treated in 100 times its weight of 2 per cent. sodium carbonate solution at 65° C. for 20 minutes. It is then rinsed in water, in alcohol, and in ether and dried to constant weight as before. This is called weight C.

4. The sample is then ashed and the ash weighed, weight D. This ash should not weigh more than 1/10 of the difference between weight B and weight C. If the silk contains a considerable amount of weighting, the treatment given in (3) above should be repeated with fresh solutions before the sample is ashed in order to obtain a low ash. A few threads of the silk treated along with the sample and ashed will show the operator whether the weighting has been removed in (3) or if the treatment must be repeated.

5.

$$\frac{\text{Weight A} - \text{Weight C} + \text{Weight D} \times 100}{\text{Weight A}} = \text{Weighting in per cent.}$$

V. *Tin Phosphate Weighted Silk.*—1. The procedure for silk which does not contain silicate is the same as that given in Section IV above, except that the following will be substituted for paragraph 3: The sample from which finishing material has been removed is soaked in 100 times its weight of 4 per cent. hydrochloric acid solution at 55° C. for 20 minutes. This is repeated with a fresh solution. The sample is then rinsed in water and soaked in 100 times its weight of 10 per cent. sodium carbonate solution at 55° C. for 20 minutes. It is then rinsed in water and the hydrochloric treatment repeated. The sample is again rinsed in water, then in alcohol and in ether and dried to constant weight, as before. This is called weight C.

VI. *Log-wood Black Weighted Silk and Silk Weighted with Lead, Zinc, or Aluminum Salts.*—1. If silicate is present, the procedure is the same as that given in Section IV except that the treatment with hydrofluoric acid is preceded by a treatment with 100 times the weight of the sample of 4 per cent. hydrochloric acid solution at 55° C. for 20 minutes repeated once with a fresh portion of the solution.

2. If silicate is not present, the procedure is the same as that given in Section V.

TYPE TESTING OF COMMERCIAL AIRCRAFT ENGINES.

ALL engines flown in licensed aircraft must be approved by the Department of Commerce as airworthy. Engines which have been tested by the Army or Navy and accepted for military purposes are approved automatically on request. Otherwise each new type of engine must pass a special test which is conducted at the Bureau of Standards.

This type testing of aircraft engines was begun at the bureau in March, 1928 (*Technical News Bulletin*, No. 133, p. 61; May, 1928, and No. 141, p. 9; February, 1929). Since that time 38 type tests have been undertaken on 26 new types of engine, several having required a second test before passing. Of these 26 types tested, 15 have passed and have received or soon will receive airworthiness certificates.

The rejection of engines has been of service to the public as may be judged from the following facts. If those engines which failed during 1928 had been put in service and flown at the speeds and horsepowers at which they were tested, they would have averaged one forced stop for each four hours of flight. How many fatalities would have resulted, no one can guess, but the number might have been large.

The test which these engines must pass at the Bureau of Standards calls for running 50 hours in ten 5-hour periods. One of these periods is at full throttle and full rated speed, the remainder at about 97 per cent. of rated speed and 90 per cent. of the rated horsepower. One engine of each type must pass this test without any serious structural failure and without more than three forced stops for any reason whatever. For each of the forced stops, if any, the engine is run an extra two hours.

The engine is then tested for horsepower at different speeds, and records are made of its performance in all important respects, such as fuel and oil consumption, kind of fuel required, etc.

Engine tests of this kind are noisy and can not well be run in residential sections. For this reason a new testing

plant has just been completed at Arlington Farms, near Hoover Field, Virginia. This plant comprises three separate testing units, each of which has a torque stand on which the engine is mounted and an observing room which houses the instruments and the testing staff. The observers are protected from injury in case of engine failure by heavily reinforced concrete walls. There are provided also (1) a shop room especially equipped for takedown and inspection of engines after test and for minor servicing during test, (2) an office and record room, (3) a furnace room providing central heating for the entire unit. The whole is housed in a concrete building so constructed as to minimize fire hazard. There is also a separate concrete building for storage of gasoline and oil, designed for protection from fire and explosion hazards.

The entire plant which will be completed in October, by the mounting of the third torque stand, is a most satisfactory modern testing unit. It was designed entirely for the purpose of running type tests of aircraft engines in which the engine is required to supply its own cooling air; hence it is not equipped with the external cooling systems required for special research problems. The latter type of equipment is available at the bureau's laboratory in Washington. On the other hand, the Arlington plant is especially designed for convenience and speed in the mounting, testing, and inspection of engines, and with three stands in operation will turn out at least one complete engine type test per week with a single staff of men. The output could be nearly doubled by the use of additional personnel should this become necessary in order to meet the demands of the rapidly growing aircraft engine industry.

NOTES FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY.*

PHOTO-VOLTAIC CELLS WITH SILVER—SILVER BROMIDE ELECTRODES. II.[1]

S. E. Sheppard, W. Vanselow and V. C. Hall.

A SYSTEM comprising an amplifier-oscillograph is described by which photographic records of photo-potential changes in the first second of illumination can be obtained. Photo-voltaic cells consisting of silver—silver bromide electrodes in various electrolytes have been studied with this arrangement, and the following factors studied: age of electrode, Svensson-Becquerel effect, halogen acceptors, electrolytes, and intermittent exposure to light. The observations on the responses in the first second of exposure support the hypothesis proposed in the first part of the paper. A more quantitative study of the initial response is planned.

EFFECT OF SOME FACTORS ON THE RING METHOD FOR DETERMINING SURFACE TENSION.[2]

A. H. Nietz and R. H. Lambert.

IN connection with work published by Nietz on orientation at solid surfaces it became necessary to adopt a convenient and rapid method for determining surface tension. The ring method, developed in most convenient form by du Nüoy, was chosen as the most suitable. In studying this method for its suitability certain results were obtained which are given here. Some of these are not new, but one in particular was singled out for study which presents some new

* Communicated by the Director.

[1] Communication No. 362 from the Kodak Research Laboratories and published in *J. Phys. Chem.* **33**: *1403. 1929.*

[2] Communication No. 379 from the Kodak Research Laboratories and published in *J. Phys. Chem.* **33**: *1460. 1929.*

aspects. This is the dependence of the ring method on contact angle, or degree of wetting of the ring by the liquid to be measured. This in particular is interesting because the reverse of the truth has met with rather wide acceptance.

Considerable data have been obtained on this effect of contact angle with a large number of organic solids. The angle was measured independently by methods previously described. A standard ring one cm. in diameter of silver wire 0.064 in. in diameter was coated with the material in question. The pull required to separate this from water was measured by means of a du Nüoy tensiometer. The tensiometer wires were calibrated in dynes. The pull (P) was plotted against the contact angle (θ). A correlation coefficient was calculated for the data, and the degree of correlation was found to be very high. Attempts were then made to set up the form of the function, and a near approximation was obtained. This had the form $F = 2lT(1 + \cos\theta)^n$, where F is the force required to pull out the ring, l the perimeter of the ring, and T the normal surface tension. This equation fails under certain conditions but fits well for certain sizes of wire. The exponent n is affected by the wire size.

This paper deals further with effects of wire size, ring diameter, and the use of spheres and of disks.

It is felt that the statement that the ring method is independent of contact angle is refuted by these results.

THE MERCURY MENISCUS.[3]

K. C. D. Hickman.

THERE are indications that perfectly pure mercury would adhere to clean glass. The failure of ordinarily purified mercury to wet glass, even in high vacuum, is due to the presence of a surface film. The alteration in shape of the meniscus and the resistance to passage of the meniscus in a narrow tube is due to this film. Some organic liquid mixtures have been found which dissolve or peptize the film

[3] Communication No. 398 from the Kodak Research Laboratories and published in the *J. Opt. Soc. Amer.* **18**: *190. 1929.*

and substitute a liquid layer which allows the mercury to pass without the meniscus sticking to the glass. The angle of contact is altered from about forty-five degrees to one hundred eighty degrees.

The organic mixtures contain two essential components, the lubricant, and the film removing substance. Examples of good lubricants are medicinal paraffin, tetra ethylene glycol methyl ether, and the alkyl esters of phthalic acid. Substances which may be added to remove the film are phenyl hydrazine, thiourea, ethyl mercaptan, and mercury di-*p*-tolyl.

Test for Methanol. HENRY LEFFMANN and CHARLES C. PINES (Am. J. Pharm., 1929, *101*, 584–586) recommend the use of a solution of potassium guaiacolsulphonate in concentrated sulphuric acid as a reagent for the detection of formaldehyde and of methanol (methyl alcohol). Formaldehyde gives a pink color with this reagent; a few drops of the unknown are permitted to fall upon the reagent which is contained in a porcelain crucible. Methanol gives the reaction after its oxidation to formaldehyde according to the procedure of the current revision of the United States Pharmacopœia. When this test is applied for the detection of the presence of methanol in ethanol (ethyl alcohol), glycerol, if present, does not interfere with the test.

J. S. H.

Manganese and Copper in Animal Metabolism. Experiments conducted by R. W. TITUS and J. S. HUGHES (*J. Biol. Chem.*, 1929, *83*, 463–467) on young rats indicate that manganese and copper are stored in the animal body when their salts, in minute amounts, are added to the ration. The daily dose of manganese was 0.1 millegram, given as the chloride. The daily dose of copper was 0.05 millegram given as the sulphate. When either manganese or copper is either fed or stored, it is effective in the utilization of iron salts by the animal for the building of hemoglobin.

J. S. H.

Alcoholic Potash and Soda. A. G. MURRAY (*J. Asso. Off. Agric. Chem.*, 1929, *12*, 309) has determined the solubility of sodium hydroxide and potassium hydroxide in methyl alcohol and ethyl alcohol. The alcohols were the ordinary laboratory reagents. The temperature was that of the room, approximately 28° C. The saturated solution of sodium hydroxide in methyl alcohol contained 23.9 grams of solute per 100 cc. of solution, corresponding to 23.6 per cent. and to a normality of 5.98. The saturated solution of sodium hydroxide in ethyl alcohol contained 13.6 grams of solute per 100 cc., corresponding to 14.7 per cent. and to a normality of 3.40. The saturated solution of potassium hydroxide in methyl alcohol contained 40.03 grams of solute per 100 cc., corresponding to 35.5 per cent. and to a normality of 7.19. The saturated solution of potassium hydroxide in ethyl alcohol contained 29.0 grams of solute per 100 cc., corresponding to 27.9 per cent. and to a normality of 5.17.

J. S. H.

THE FRANKLIN INSTITUTE.

STATED MONTHLY MEETING, OCTOBER 16, 1929.

The monthly meeting of the Institute was called to order by the President, Mr. Nathan Hayward, at eight-fifteen p.m.

The Secretary announced that the last meeting of the Institute had been the annual Medal Day meeting, held on May sixteenth. He stated that the minutes of that meeting and the full account of the Medal Day exercises had been printed in the Journal for June and July respectively. He then moved that these minutes and account of the Medal Day exercises be approved as printed. The motion was seconded and unanimously carried.

The President, Mr. Hayward, made a short talk, describing some of his experiences during the last summer, which showed the high standing The Franklin Institute has in scientific circles in Europe. He closed with an appeal to the membership to know the Institute and to make it known to their friends.

The President then introduced as the speaker of the evening, Dr. John A. Miller, Vice-President, Professor of Astronomy, and Director of the Sproul Observatory, Swarthmore College, who spoke very interestingly on "Gleamings of Recent Eclipses."

The lecture was followed by a discussion in which several members of the audience participated.

The meeting adjourned at nine-thirty-five p.m., with a rising vote of thanks to Dr. Miller for his delightful talk.

HOWARD MCCLENAHAN,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, October 2, 1929.)

HALL OF THE INSTITUTE,
PHILADELPHIA, October 2, 1929.

DOCTOR THOMAS D. COPE *in the Chair.*

The following report was presented for final action:

No. 2899: Hardened Metallic Drive Screw.

This report recommended the award of the Certificate of Merit to Mr. Heyman Rosenberg, New York City, N. Y., "In consideration of the successful modification of screws, consisting of hardening the threads, thus permitting them to thread their way when driven or turned into the material to be joined, and the invention whereby the diameter of the body at the base of the thread is less than that of the cylindrical end."

The following report was presented for first reading:

No. 2861: Car Retarder System.

GEO. A. HOADLEY,
Secretary to Committee.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, October 16, 1929.)

RESIDENT.

MR. CHARLES B. EGOLF, Chemical Engineer, Charles Lennig and Company, Bridesburg, Pa. For mailing: 2803 North Broad Street, Philadelphia, Pa.

MR. RICHARD H. OPPERMANN, Librarian, United Gas Improvement Company, 112 North Broad Street, Philadelphia, Pa.

MR. WILLIAM H. SCHAEFFER, Engineer, Atwater Kent Manufacturing Company, Philadelphia, Pa. For mailing: 6347 Chew Street, Germantown, Philadelphia, Pa.

NON-RESIDENT.

MR. EDGAR S. NETHERCUT, Secretary, Western Society of Engineers, 205 West Wacker Drive, Room 1200, Chicago, Illinois.

MR. HARDEN FRANKLIN TAYLOR, Vice-President for Scientific Research, Atlantic Coast Fisheries Company, 111 John Street, New York City.

CONTRIBUTING MEMBERSHIP.

MR. J. C. MELCHER, Salesman, Leeds and Northrup Company, 4901 Stenton Avenue, Philadelphia, Pa. For mailing: 5531 Pulaski Avenue, Germantown, Philadelphia, Pa.

MR. G. A. PERLEY, Chief, Chemical Division, Development Department, Leeds and Northrup Company, Philadelphia, Pa.

MR. H. W. LANDENBERG, American Engineering Company, Philadelphia, Pa.

NECROLOGY.

Dr. Felix A. Boericke, Bryn Athyn, Pa.
Mr. John F. Conaway, Philadelphia, Pa.
Mr. John W. Hornsey, New York City.
Mr. T. E. Mitten, Philadelphia, Pa.
Mr. Thomas E. Murray, New York City.

LIBRARY NOTES.

RECENT ADDITIONS.

BRICOUT, PIERRE. Ondes et Électrons. 1929.

DUNCAN, RUDOLPH L., AND CHARLES E. DREW. Radio Telegraphy and Telephony. 1929.

Engineering Foundation. Popular Research Narratives. Volume III. 1929.

FORD, LESTER R. Automorphic Functions. 1929.

GAUSS, CARL FRIEDRICH. Werke: Bd. 2, Nachtrag zum ersten Abdruck; Bd. 10, erste Abt.; Bd. 10, zweite Abt., Abh. 1, 4, 5; Bd. 11, erste Abt; Bd. 11, zweite Abt., Abh. 1–3; Bd. 12. Six volumes. 1876–1929.

GEIGER, H., AND KARL SCHEEL, editors. Handbuch der Physik: Bd. XXI. 1929.
HAGUE, B. Electromagnetic Problems in Electrical Engineering. 1929.
HAUSBRAND, E. Evaporating, Condensing, and Cooling Apparatus. Trans. from the 2d revised German edition by A. C. Wright. 4th English edition, revised and enlarged by Basil Heastie. 1929.
HEALY, KENT TENNEY. Electrification of Steam Railroads. 1929.
HOLTMAN, DUDLEY F. Wood Construction: Principles, Practice, Details. 1929.
HOOL, GEORGE A., AND NATHAN C. JOHNSON, editors-in-chief. Handbook of Building Construction. Second edition. Two volumes. 1929.
HULSE, EDWARD PIERCE. Arc Welding. Lincoln Prize Papers Submitted to the A. S. M. E. 1929.
JEANS, SIR JAMES. The Universe Around Us. 1929.
KOLTHOFF, I. M., AND H. MENZEL. Volumetric Analysis. Volume 2. Authorized translation by N. H. Furman. 1929.
LISTER, WALTER. Practical Steelmaking. 1929.
MARKS, PERCY L. Thermometric Conversion Chart. 1927.
NORTON, F. H. The Creep of Steel at High Temperatures. 1929.
PAGE, VICTOR W. Modern Aviation Engines. Two volumes. 1929.
Philadelphia Sesqui-Centennial International Exposition, 1926. Record Based on Official Data and Departmental Reports by E. L. Austin and Odell Hauser. 1929.
PRITCHARD, J. LAURENCE. The Book of the Aeroplane. Second Edition. 1929.
ROBERTS, J. K. Heat and Thermodynamics. 1928.
TRACY, JOHN CLAYTON. Stresses Statically Determined. 1929.
WIEN W., AND F. HARMS, editors. Handbuch der Experimentalphysik: Bd. IX 2 Teil; Bd. XX, 2 Teil. Two volumes. 1929.
YANCEY, LEWIS A. Aerial Navigation and Meteorology. 1929.
YOUNG, C. R. Elementary Structural Problems in Steel and Timber. 1929.

BOOK REVIEWS.

THEORETICAL MECHANICS. AN INTRODUCTION TO MATHEMATICAL PHYSICS. By Joseph Sweetman Ames, Provost, and Sometime Director of the Physical Laboratory and Professor of Physics, the Johns Hopkins University and Francis D. Murnaghan, Professor of Applied Mathematics, the Johns Hopkins University. ix—462 pages, 39 figures, 8vo. 1929, Ginn and Company, Boston. Price $5.

With the introduction of the more recent theories of physical science such as the Quantum Theory, Relativity, and Wave Mechanics embodying the Theory of Matrices, the use of mathematical physics has become more and more extensive and considerable impetus given to the study of theoretical mechanics. The compilation of this book has been conducted with the object of providing students of mathematics, physics and chemistry with a source of information concerning the newer mathematical processes and their application to some of the present-day scientific theories and experiments. In order that this knowledge may be acquired without the aid of an instructor, the authors have been careful to include all

the steps necessary for the proof of theorems and formulas. As a further aid, each chapter is supplied with a number of problems and their solutions while a list of exercises are to be found at the ends of the chapters. The book starts out with a chapter on Vector Analysis. Following this are the mathematical treatments of such subjects as, the Motions of a Rigid Body, the Dynamics of Particles and Groups of Particles, Central Forces including Newton's Law of Universal Gravitation, Impulsive Forces, Gyroscopic Theory, General Dynamical Theorems, the Principle of Least Action and of Least Constraint, Wave Motion, the Lorenz-Einstein Transformation and Tensors. An introduction to the relativity concept will be found in the chapter on the Einstein-Lorenz Transformation. The transformation itself being the mathematical process of interpreting a motion observed in one reference system in terms of observations made in another reference system upon this selfsame motion. As a consequence, there is evolved the well known relative motion equations involving the velocity of light. The last chapter is concerned with a definition of physical quantities in the terms of the fundamental quantities, mass, length and time. The book contains numerous references on closely related subjects for the benefit of the student wishing to pursue his studies further.

T. K. CLEVELAND.

THE UNITED STATES COAST AND GEODETIC SURVEY, ITS WORK, METHODS, AND ORGANIZATION. Special Publication No. 23 (1928 revised edition). 130 pages, illustrations, 8vo. Washington, Government Printing Office, 1928.

The compilation and publication of precise data on the coast line and its approaches of interest to navigators is obviously of the greatest importance to maratime nations. That service in this country had its inception a little more than a century ago under the name of Coast Survey; and about fifty years ago, the bureau was enlarged and its designation became, as it is known today, the Coast and Geodetic Survey. Primarily, the activities of the Bureau are directed toward the production of charts of the coast line and other tide-water localities which may be used with certainty by navigators. These charts are also valuable for military defense, harbor improvement, the study of physical hydrography and the problems of oceanography. The field activities of the Coast and Geodetic Survey are carried on to supply the information needed to prepare these charts and supplementary information of importance to the mariner in book and tabular form which cannot conveniently be placed on a chart.

As the title indicates, this volume is an account of the work of the Bureau, the methods which are employed in carrying it on, the equipment, and organization. There are seventeen chapters, each one devoted to some particular topic and mode of procedure with numerous well-executed illustrations. The main object of a geodetic survey is to furnish the necessary control for all other surveys. This includes the determination of the relative positions of some principal points of reference upon which to base the work. It involves the measurement of base-lines and the measurement of the angles of the triangulation system. In that connection are discussed the methods of the Bureau in the determination of time, latitude, longitude and azimuth, and needless to say, in keeping with the most advanced practice in the art, with occasional reference to superseded methods. Thus, since 1922, radio time signals are employed in the determination of longitude.

Previously, the electric telegraph was used for that purpose, and still earlier, a chronometer indicating the time of the base meridian. Among the measuring instruments the modern "invar" tape which is now used is regarded as a satisfactory solution of the great problem of base-line measurement.

Under "hydrography" we learn that the recent echo-sounding method is rapidly superseding all others. Again there is the "wire-drag" which reveals with a certainty unattainable by any other method all of the hidden dangers to navigation that may be in the pathway of ships. A multiplicity of other equally representative topics are treated with analytical comparisons and comments on appliance and procedure. It is a comprehensive and illuminating account.

L. E. P.

CHEMISTS' POCKET MANUAL. By Richard K. Meade, M.S. Fourth edition. 533 pages, illustrations, 16mo. Easton, Chemical Publishing Company, 1929. Price, $5.00.

Works of this kind are being published in many of the sciences devoted to practical purposes. They represent a very large amount of labor in collating, composing and checking. They are exceedingly useful and are, therefore, quite popular. This volume will be in constant use in the analytical laboratory whether devoted to engineering, metallurgy or general chemistry. The book is compact, printed in clear type with numerous tables containing altogether a very large amount of useful data.

H. L.

MANUAL OF SECOND AND THIRD ORDER TRIANGULATION AND TRAVERSE. By C. V. Hodgson, Hydrographic and Geodetic Engineer, United States Coast and Geodetic Survey. Special publication No. 145. v–226 pages, illustrations, 8vo, paper. Washington, Department of Commerce, U. S. Coast and Geodetic Survey, 1929. Price, sixty cents from Supt. of Documents, Washington, D. C.

Needless precision entails both unnecessary cost and unnecessary expenditure of time, and in any enterprise in which measurements of the same nature and various degrees of precision may be applied, it is essential for economy of operation to prescribe methods of procedure that harmonize with this varying refinement. This systematic grading of procedure in accordance with prescribed limits of error is an important feature in the extensive and varied operations of geodesy. The United States Coast and Geodetic Survey employ ordinarily three grades of vertical and horizontal control which are designated, first order, second order and third order, respectively, the first named being the most accurate.

This special publication contains the specifications used by the Bureau for executing second-order traverse and describes the methods to be employed and how computations, both field and office, are to be made. The topical headings are: Reconnaissance, Second and Third Order Triangulation; Second and Third Order Base Measurement; Second and Third Order Traverse; and Astronomical Azimuths, Constants, Formulas and Tables. Under these captions are included a comprehensive collection of methods, data, equipment, and procedure which are adopted to insure the precision of a survey in accordance with specifications of the limits of error of its various components. The methods described, the

author states, are the results of gradual changes extending over many years and are due to the suggestions and investigations of many persons, among whom are particularly mentioned, W. F. Reynolds, senior mathematician; W. D. Sutcliffe, associate mathematician; and C. H. Sarck, senior mathematician.

The manual is intended to supplement text-books teaching the basic principles of control surveys with a detailed account of modern requirements on second-order horizontal control surveys, and approved practices of the Coast and Geodetic Survey. L. E. P.

CHEMICAL ENGINEERING CATALOG. Fourteenth Annual Edition, 1205 pages, illustrations, quarto. New York, The Chemical Catalog Company, Inc., 1929. Prices adjusted to special conditions as indicated in the volume.

This publication has been noticed as it appeared in the issues of the Journal and it is necessary here only to record that the present edition maintains the character of the work as established in its earlier publications and constitutes a very valuable summary of the chemical engineering manufacturing in this country. The classified directory has been further enlarged and contains the listings of more than 2000 manufacturers. Its use to those engaged in purchasing the materials of chemical engineering is very great and the manner in which the publishers keep in touch with those who use the book is highly commendable. The information bureau maintained by the publishers for many years has been doing excellent service to its customers. More than 2600 books are listed in the technical and scientific books section. Information is also given concerning the American Chemical Society's Monographs. The book is printed in excellent form and very liberally illustrated. The present edition has been enlarged about two score pages. Full and detailed information concerning the products of the firms using the spaces is given in individual pages and these should always be consulted. H. L.

EXACT COLOUR MATCHING AND SPECIFYING. By L. Blin Desbleds, Colour Technologist, Member of the Textile Institute, Member of the Society of Dyers and Colourists, etc. 116 pages, illustrations, 21 x 13 cm., paper. Paris, Technological and Industrial Service. Price, $1.00.

The similarity of color between two surfaces, when judged by the eye alone, is always uncertain however well-proved the normality of the observer's color-vision may be. Whatever the apparatus employed in carrying out the processes of color measurement, the eye until recently has been the final component of the optical system with which the magnitude of the radiation is determined. There is now, thanks to progress in photoelectronic apparatus, a substitute for the eye which is sensitive, invariable in its functioning, and always gives concordant results; namely, the photoelectric cell. The photoelectric cell has been incorporated by Toussaint in an apparatus known as the "Toussaint Electric Photocolorimeter" by means of which substantially exact determinations of spectral-color content may be made of a given mixed color. The only part played in the process by the human eye is limited to taking galvanometer readings. A small number of such readings provide figures which specify the color under examination in terms of definite wave-lengths.

In this résumé and handbook on color matching, the author explains the modern conception of the nature of color phenomena, the relation of color to white light, and curves of color-intensity against wave-length. How these curves are obtained from the photo-cell colorimeter and how values of the intensity at characteristic wave-lengths may be employed to accurately describe a given color are explained at length in simple and precise language. The colorimeter is fully described and illustrated by diagram and a half-tone plate.

While of general application the work is addressed more particularly to the textile colorist and considerable space is devoted to matters relating to the manipulation of dyestuffs for a desired effect. With regard to the optical density of a dyestuff as a function of its concentration, the methods and equations which have become familiar in sensitometry since the investigations of Hurtur and Driffield are employed in defining color-quality. Further specific methods of procedure in the preparation of dye baths and other matters of interest in dye-house procedure are included.

Not alone textile colorists, but all others who seek sound information on the principles of color composition and practical methods of color measurements will find this work one of rare interest and a convincing guide.

LUCIEN E. PICOLET.

SPARKING OF STEEL. Facts which Everybody Using Steel Should Know and Use. By E. Pitois, Graduate of Ecole Polytechnique, Chief Inspector of the Construction Section of the Governmental Air Service, with a preface by General Hirschauer, Former Chief of Military Aviation, Former Commander of the Second Army, Chairman of the Aviation Committee of the Senate. Translated from the French and enlarged by John D. Gat, Research Metallurgist, American Sheet and Tin Plate Company. ix–89 pages, illustrations, 8vo, cloth. Easton, The Chemical Publishing Co., 1929. Price, $2.00.

Those who have had occasion to grind modern steel cutting-tools for machining operations are familiar with the markedly characteristic difference in the color of the spark-stream between the common type of carbon tool steel and tool steel of the self-hardening variety. The former yields bright yellow sparks, the latter, sparks of a less luminous reddish hue. Doubtless only to few, among the numberless technologists to whom these differences of coloration are familiar has it occurred that a closer examination of the spark-stream will disclose peculiarities characteristic of the composition of the material. It is to M. Pitois that the inspiration has come to classify these peculiarities and utilize them as a proximate method of analysis for the commercial classification of steels. In this account of the method he describes its evolution, its technique and its limitations.

The estimation of the carbon content of steels by examination of the fracture has long been in vogue, and experienced steel-makers have shown an ability to classify steels according to carbon-content within surprisingly narrow limits. Like all other methods of testing, except brinelling, it is only applicable to representative samples and not to each individual piece. Herein, the author says, lies the inestimable advantage of "sparking." Every one of the individual pieces of a lot, be they bars, sheets, tubes or castings may be checked in a few seconds. The apparatus which the author recommends for this purpose is a light portable grinder with a wheel $1\frac{1}{2}$ inches in diameter and $\frac{1}{4}$ inch thick and having a speed

of 12,000 r.p.m. Obviously, with such a tool, contact with the ends of bars, for instance, may be made with very little handling.

To effectively proceed with a test by sparking, it is essential that the operator fix in mind the particular forms which the sparks assume as well as their color. To that end, the work contains over a score of photographs of spark streams with legends of the grades of steel from which they were made. Fragmentary enlargements with the photographs define clearly the patterns of the spark streams shown; carbon-steels, cast-irons, and alloy-steels are included. The photographs are reproduced in half-tone. A short account of the technique of producing the photographs is given in an appendix. Appendix II deals with a variation of the method which consists in permitting the spark-stream to impinge upon a glass plate covered with moist gelatin to which the particles of the abraded material adhere. Several photographs of incrustations so made accompany the text. In appendix III, the author gives an account of his investigations on spark-streams maintained in other gases than air.

A fourth and final appendix of rare interest is on spark-testing as it is conducted in the United States, which is an account of its application under the direction of Mr. John A. Houtz of the United Alloy-Steel Corporation, Canton Ohio. Mr. Houtz describes the manipulative procedure at length pointing out the advantages and the limitations of the method. As indicative of the possibilities of sparking he mentions several instances. Referring to one of these he says: "In one of the largest plants in the country, a mixup involved 125,000 finished tubes. Their identity was completely lost and to separate them, a carbon determination had to be run on every piece. Conservative estimates of laboratory costs give an average cost of carbon determination around fifty cents. The plant laboratory, considering the time-element, of course could not handle the situation. Sparking was resorted to and $62,500 worth of analysis was replaced by 14-days work of the writer and his assistant."

M. Pitois has given in this volume an account of a method of classifying steels of great simplicity and unusual promise which should be of widespread interest in the metallurgical industries. LUCIEN E. PICOLET.

TIN. ITS MINING, PRODUCTION, TECHNOLOGY AND APPLICATIONS. By C. L. Mantell, Ph.D. American Chemical Society Monograph Series. 366 pages, illustrations, 8vo. New York, The Chemical Catalog Company, Inc., 1929. Price, $7.00.

This is one of the volumes of the American Chemical Society monographs of which so many have already been published, covering a very wide field of both theory and practice in chemistry, constituting a very valuable library on these subjects. The present volume is devoted to a metal which has many important uses and which would be much more widely applied and serve many purposes if it occurred in greater abundance. In its metallic state it has brilliancy, resistance to ordinary corrosion, is very malleable and of low melting point. It is alloyed readily with several of the common metals especially copper and a considerable variety of valuable alloys are produced in this way. It seems to have been employed in alloy form before the period of which we have written records.

Tin is not known to occur native except in very small amount and its ores are found in practical quantities only in a few localities. The metal was probably

obtained originally by a crude method of smelting its ores with logs of wood, the molten metal being collected in a hole in the ground. Mines in Cornwall have been for many centuries a source of supply of the tin oxide known as cassiterite or tin-stone. This is really the important source of the metal. Tin has been familiar in the household for many years in the form of tin-plate, which being merely iron coated with tin, is subject to certain dilapidation inasmuch as the iron being more positive than the tin suffers rapid corrosion if a portion of the latter metal is scratched off. The practical condition is just the reverse of that in the so-called galvanized iron, the coating metal, zinc, being more positive than the iron bears to a certain extent the brunt of corrosion.

Devoted as it is to one metal, the book covers all important phases of its metallurgy. A few introductory pages give some facts in the history: the physical chemical properties are presented at length, the types of ore and the character of the deposits thereof are described. These data are followed by methods of extraction, and practical questions concerning the operation of the refinings. The newer methods of gas and electrolytic refining are fully presented. The older method of producing tin plate was by dipping, but electrolytic methods of depositing are now in vogue and are described. A chapter is devoted to the alloys, which are very numerous and of great importance. The standard methods of manufacturing tin plate by dipping receives notice in a special chapter. Considerable attention is given to the subject of corrosion of tin and of the relation of tin containers to foods. The latter is of much importance and interest, the discarded tin-can is a prominent feature to our modern civilization. A special table of the relative value of tin in the canning industry is given at the close of the chapter on corrosion. Some note is also made of the action of photographic solutions upon tin containers, the commercial salts are duly considered, and a chapter is given to recovery of tin from scrap and also an outline of analytical methods.

We have here, therefore, a highly interesting and valuable contribution to the chemistry of a useful metal.

HENRY LEFFMANN.

PUBLICATIONS RECEIVED.

Mechanical Equipment of Buildings, volume I. Heating and Ventilation. A reference book for engineers, architects and contractors by Louis Allen Harding and Arthur Cutts Willard. 2d edition, revised and enlarged, 963 pages, illustrations, 8vo. New York, John Wiley & Sons, Inc., 1929. Price $10.00.

Introduction to Physical Optics, by John Kellock Robertson. 422 pages, illustrations, 8vo. New York, D. Van Nostrand Company, 1929.

The Electromagnetic Field. Max Mason and Warren Weaver. 390 pages, illustrations, 8vo. Chicago, The University of Chicago Press, 1929. Price $6.00.

Tin, its Mining, Production, Technology, and Applications, by C. L. Mantell, Ph.D., American Chemical Society Monograph Series. 366 pages, illustrations, 8vo. New York, The Chemical Catalog Company, Inc., 1929. Price $7.00.

The Chemists' Pocket Manual. A practical handbook containing tables,

formulas, calculations, information, physical and analytical methods for the use of chemists, chemical engineers, assayers, metallurgists, manufacturers and students, by Richard K. Meade. 4th edition, 533 pages, illustrations, 16mo. Easton, Pa., The Chemical Publishing Company, 1929. Price $5.00.

Sparking of Steel. Facts which everybody using steel should know and use, by E. Pitois. Preface by General Hirschauer. Translated from the French and enlarged by John D. Gat. 89 pages, plates, 8vo. Easton, Chemical Publishing Company, 1929. Price $2.00.

Chemical Engineering Catalog, 1929 (fourteenth annual) edition. Collected, condensed and standardized catalog data of equipment, machinery, laboratory supplies, heavy and fine chemicals and raw materials. . . . 1205 pages, illustrations, quarto. New York, The Chemical Catalog Company, Inc., 1929. Price $10.00.

Newton, Maupertius et Einstein. Reflexions à propos de la relativité, par F. Prunier. 79 pages, 8vo. Paris, Librairie scientifique Albert Blanchard, 1929. Price 12 francs.

La Nouvelle Mécanique des Quanta, par George Birtwistle. Traduction augmentée de 4 appendices par les Traducteurs, M. Ponte et Y. Rocard. Preface de M. Jacques Hadamard. 333 pages, illustrations, 8vo. Paris, Librairie scientifique Albert Blanchard, 1929. Price 75 francs.

Memoranda of Toxicology partly based on Tanner's Memoranda of Poisons, by Max Trumper, B.S., A.M., Ph.D. Second edition, 214 pages, 16mo. Philadelphia, P. Blakiston's Son & Co., Inc., no date.

CURRENT TOPICS.

The International Relationship of Minerals. SIR THOMAS HOLLAND. (*Nature*, Aug. 3, 1929.) This address was delivered by the president of the British Association for the Advancement of Science at Johannesburg, South Africa, on July 31, 1929. Instead of speaking upon the outstanding problems in the special field of petrology where he might well be regarded as an authority he departs from all questions of narrow scientific interest and discusses "the special ways in which the trend of mineral exploitation since the War has placed a new meaning on our international relationships."

The legends attached to the names of Isis, Cybele, Demeter and Ceres "made it likely that a woman—tied for long periods to the home-cave—rather than a man, was the one who first discovered the possibility of raising grain-crops by sowing seed. Compared with this economic application of observational science, the later inventions, which seem so important to us—explosives, printing, the steam engine—were but minor incidents in the evolution of civilised activities." With agriculture new cares arrived. Village groups were formed and later tribes arose. "Then afterwards, long afterwards—indeed, up to historically recent times—national boundaries became extended or were fought for, but still mainly because agricultural products in some form were a necessity for the maintenance of communal life." British traders went to India for agricultural products and British India remains chiefly agricultural. "Even in South Africa which produces half the world's supply of gold, the value of the metal is still less than that of the pastoral and agricultural products." Again and again the lure of gold has led to conquest and colonization in lands whose agricultural resources later far exceed their mineral wealth.

The industrial revolution in Great Britain accelerated the development of the mineral resources of that country, and was conditioned by the occurrence of suitable minerals in England. For the first half-century of the industrial revolution Great Britain furnished its own iron, copper, zinc, lead and tin, but, after Bessemer's announcement of his process at the Cheltenham meeting of the British Association in 1856 and the expansion of steel production that followed it, it became necessary to seek abroad non-phosphoric iron ore and the accessory ores. When Thomas and Gilchrist made it possible to use phosphoric ores their process was of advantage,

not to Britain, but to the United States and to Germany. Thus the use of the phosphoric iron ore deposits of Alsace-Lorraine put Germany in a position to try the fortunes of war in 1914.

In 1888 Sir Robert Hadfield brought out his special manganese-steel and opened the way for the production of other ferro-alloys. Thus commercial amounts of vanadium, tungsten, molybdenum, aluminium, chromium, cobalt and nickel were needed. From the beginning of the twentieth century no nation could be self-contained in the matter of metals, though the extent of the interdependence was not realized until the war made it clear. "Although the wolfram deposits of South Burma were worked almost entirely by British companies, the whole of the mineral went to Germany for the manufacture of the metal, tungsten, which was an essential constituent of high-speed tool steel. Sheffield still occupied a leading place in the production of this variety of steel, but was dependent on Germany for the metal, which the Germans obtained mainly from British ore. Under the compulsion of necessity, and without consideration of commercial cost, we succeeded before the middle of 1915 in making tungsten, whilst Germany, failing to obtain an early and favourable decision in war, used up her stocks of imported ore and turned to the Norwegian molybdenum as a substitute, until this move again was partly countered by our purchase of the Norwegian output. Germany then found that she wanted ten times more nickel than Central Europe could produce; so she imported her supplies from the Scandinavian countries, and they, being neutral, obtained nickel from another neutral country, where the Canadian ores—the world's main source—had hitherto chiefly been smelted and refined. We thus realised, not only our dependence on other lands for the essential raw minerals, but also we had the mortification of finding that, through our own previous shortcomings in the metallurgical industries, we were compelled to face lethal munitions made of metal obtained from our own ores."

The consumption of metals is going on at an accelerated rate. "During the first quarter of this present century alone, the world has exploited and consumed more of its mineral resources than in all its previous history, back to the time when eolithic man first shaped a flint to increase his efficiency as a hunter." The production of steel in the United States was 69,000 tons in 1870 and in 1928 45,000,000 tons. For the world as a unit the depletion of its mineral resources is not yet alarming. The miner works only such deposits as contain the metal in sufficient concentration to make it profitable and ores vary greatly from place to place in their richness in metal. Nickel ore is widely distributed and relatively abundant, yet "under the present state of mining and metallurgical practice the deposits in the

world worth working for nickel can be numbered on the fingers of one hand, and nine-tenths of our supplies come from a single district in Canada. As the result of estimates made for certain common metals the striking conclusion is reached that "we shall not be far from the average in assuming that we shall never recover more than about one-millionth of the total that lies within workable distance from the surface of our accessible dry land. Another conclusion, based on a similar group of calculations, shows that our greatest total tonnages are not contained in the rich deposits, but in those of low grade. It follows, therefore, that every advance in metallurgical science and in mining technology that makes it possible to work our low-grade ores adds appreciable to the actuarial value of civilisation; for our mineral resources can be worked once, and once only in the history of the world; and when our supplies of metalliferous ores approach exhaustion, civilisation such as we have now developed during the last century must come to an end." There is room for improving both the processes of mining and of treating the ore and the most promising direction is by substituting machines for hand labor. This in itself tends to limit operations to extensive deposits and to restrict mining to a relatively small number of localities.

The United States does not have the minerals it needs for peace and for war. Nor is even the widely extended British Empire self-contained in this regard. An instructive list of minerals in relation to the Empire is given:

"1. Those for which the world now depends mainly on the Empire:—Asbestos, china clay, chromite, diamonds, gold, mica, monazite, nickel and strontium.

"2. Those for which we have enough and to spare:—Arsenic, cadmium, cobalt, coal, fluorspar, fuller's earth, graphite, gypsum, lead, manganese, salt, silver, tin and zinc.

"3. Those in which we could be self-contained if necessary:—Bauxite, barium minerals, felspar, iron ore, magnesite, molybdenum, platinum, talc, tungsten and vanadium.

"4. Those for which we are now dependent on outside sources:—Antimony, bismuth, borates, copper, petroleum, phosphates, potash, pyrites, quicksilver, sulphur and radium."

The British Empire and the United States together are the sources of more than two-thirds of the world's annual consumption of minerals, which amounts to 2,000,000,000 tons. Though each of these countries is so rich in minerals neither has enough of all kinds to supply its own needs. Indeed the two with all resources pooled would have to go to other countries for a few minerals. Thus there is an imperative need for international interchange of minerals.

When attention is fixed on the occurrence in countries of mineral deposits sufficiently important to support metallurgical units to the neglect of poorer concentrations, a different opinion must be formed of the provision of minerals in different countries from that held a few years ago. "The critical investigations made by mining geologists, especially since the War, tend, with a striking degree of unanimity, toward recognizing the remarkable circumstance that China, as well as other countries of the Far East, is deficient in those essential deposits of minerals on which our mechanised form of civilisation is based." For this reason the "yellow peril" and the "challenge of Asia" cease to be terms of dread. The importation of lacking minerals is limited by the quantity of exportable materials for payment.

Essential minerals are not distributed uniformly over the earth. North America and Western Europe have more than their share of such minerals. "Nine-tenths of the coal, two-thirds of the copper, and as much as 98 per cent. of the iron-ore consumed by the world come from the countries that border the North Atlantic." The industrial revolution beginning in Great Britain faded away toward the Slavic east and the Latin south, by reason of the lack of important minerals. "Thus in these two main areas, separated by the Atlantic Ocean, a family of industries based on mineral resources has arisen to dominate the world. Political control, which follows industrial dominance must lie with the countries that border the North Atlantic. The only two nations that can fight for long on their own natural resources are the British Empire and the United States." Sir Thomas Holland reaches the climax of his address by making the suggestion that these governments unite in refusing to export mineral products to any country violating the Kellogg pact. A somewhat similar proposal was made in the Senate of the United States by Senator Capper, who would forbid the export of "arms, munitions, implements of war or other articles for use in war." It would be much easier to determine whether in time of war an article came under the head of mineral products than to decide whether it could possibly be used for the conduct of war. "If they (Great Britain and the United States) agree in refusing to export mineral products to those countries that infringe the Kellogg pact, no war can last very long."

G. F. S.

Cosmical Magnetic Phenomena. S. CHAPMAN. (*Nature*, July 6, 1929.) This is the Rouse Ball Lecture, delivered at Cambridge, England, on May 31, 1929. Of all astronomical bodies it is only the sun and the earth that have been observed to possess magnetic

fields. The magnetism of the earth has been the subject of study for more than three centuries since Gilbert in 1600 published his treatise, while Hale on Mount Wilson no more than twenty-one years ago detected the magnetism of the sun. All that is known of the sun's magnetism comes from this single observatory.

The magnetism of the earth acts directly upon measuring instruments, but that of the sun can be got at only indirectly. "It depends on the influence, called the Zeeman effect, which the field exerts on atoms emitting or absorbing light. Certain lines in the solar spectrum are split up, or broadened, by an amount which indicates the magnetic intensity at the sun's surface. From this it is easy to calculate the maximum possible intensity of the sun's magnetic field near the earth, and to show that it is too small to be measured directly." As the sun is a typical star it may well be that other stars have magnetic fields and that later they may be detected. At the present time, however, it is difficult enough to deal with the solar field.

Do the moon and the planets have magnetic fields? Since the moon is the source of no light and has no atmosphere to absorb light the Zeeman effect would not reveal any magnetic field did one actually exist. Moreover it is uncertain whether the effect could be measured on any planet. The indirect method of the Zeeman effect being ruled out the lunar and planetary fields must be detected by direct methods if they are discovered at all. It may be that eventually they may be seen to deflect streams of charged particles coming from the sun but at present it is wiser to examine whether at the earth any possible magnetic field due to another member of the solar system could be shown to exist. It is known that a daily variation of the terrestrial magnetic field, due to the moon, exists, but is an indirect effect of the tides set up in the atmosphere by the action of the moon. No variation of the earth's field such as the moon might cause directly has been found, nor have any direct planetary effects been discovered. Thus up to the present time cosmical magnetic phenomena are limited to the earth and the sun. For their elucidation there are needed (*a*) measurements, accurate detailed and long-lasting, (*b*) the reduction of these measurements to a concentrated body of facts, (*c*) the explanation of the facts according to general physical laws. Observations have been accumulated in many observatories. The Carnegie in her long voyages has recorded magnetic data on the surface of the ocean. The herculean task of digesting the observations is incomplete and "most of the problems of cosmic magnetism remain unsolved." Unfortunately the enormous scale of the phenomena almost precludes the testing of hypotheses by experiment.

Gilbert of Colchester in 1600 showed that the earth is a great magnet acting like a magnetized sphere. The magnetic axis is at an angle of 12° with the axis of rotation of the earth. For about three centuries the changes in the direction of the earth's magnetic force have been measured in a few localities. Observations made in London since 1540 show rather regular and perhaps periodic changes in the direction of both declination and inclination. It looks as if, after five centuries, these will return to their sixteenth century values. "The earth's magnetization seems to have decreased by about 5 per cent. during the century for which observations of the intensity are available: at present the decrease is proceeding most rapidly in the southern hemisphere."

"On the basis of our present knowledge, it is impossible to guess or predict the future course of the earth's magnetism." Students of terrestrial magnetism with their 300 years of observations are at a disadvantage in comparison with astronomers possessing data milleniums old and with geologists having rock records of great age. Folgheraiter in Italy and Mercanton in Switzerland have, however, studied the magnetization of lava and other rocks retained from the time of their solidification and have inferred the direction of the earth's field at that epoch.

About 1840 Gauss applied the theory of potential and spherical harmonic analysis to the earth's field. By this method it has been shown that the magnetic field at the surface of the earth is almost entirely due to causes lying within the earth, at most 3 per cent. of the field being attributable to external causes. There may be a small part due to vertical currents and having no potential. The intensity of the earth's magnetic field varies inversely with the cube of the distance from its center. At 4,000 miles above the earth's surface it amounts to one-eighth of its value at the surface. Thus the terrestrial field is still of appreciable strength thousands of miles above us, and tubes of force extend far beyond the atmosphere.

Solar Magnetism.—In the sun's atmosphere the Zeeman effect can be measured at different levels on lines of different elements. Thus Hale and his co-workers have found a rapid decrease of intensity with elevation. "The measured reduction (from 50 to 10 gauss for the polar intensity) is in the ratio 5 to 1 and extends over a linear distance of only about 50 km." If the same law of decrease held as on the earth it would be necessary to go up more than 1,000,000 km. to get the same diminution. Whether the reduction continues cannot be told because 10 gauss is the limit at present of possible measurement. In contrast to the earth "few or no tubes of magnetic force can pass from the sun's atmosphere into outer space."

Like the terrestrial field the solar field is almost symmetrical about an axis. On the sun this is inclined at 4° to the axis of rotation. A feature of much theoretical interest is that the polarity of the earth and of the sun are the same with relation to their directions of rotation. "The earth's field including its irregularities, rotates at the same speed as the nearly rigid earth, whereas the sun's field and magnetic axis rotate more slowly than the solar surface, the respective periods of rotation being about 31 days and 26 days. The polar intensity of the earth's field is about 2/3 of a gauss, while for the sun it is estimated to be 50 gauss." The sun has not only a general magnetic field but also local fields connected with sunspots, where the intensity reaches 3000 gauss. Sunspots usually come in pairs of opposite magnetic polarity, the line joining them running parallel to the sun's equator. "The polarity of the leading spots of pairs in one hemisphere (northern or southern) is the same as that of the following spot in the other hemisphere." The number of sunspots changes in an eleven-year cycle. When a fresh cycle appears the polarity that prevailed in the former one is reversed. "The leading spots in both hemispheres have the polarity which in the preceding cycle characterised the leading spots in the other hemisphere." The magnetic sunspot cycle is therefore 22 years long. "A beautiful qualitative theory of this remarkable series of phenomena has been outlined by Bjerkenes, and awaits quantitative development."

Many hypotheses have been framed to account for the earth's magnetism, but none has been found satisfactory. Can the earth's field be due to this body's being magnetized entirely or in part as a lodestone is magnetized? Iron and other magnetic substances lose their magnetism at their critical temperatures which are reached at 20 to 30 km. below the surface. Magnetic deposits above this depth account for disturbances of the terrestrial field but do not account for the general field. It was thought that the pressure at great depth might raise the critical temperature, but the Geophysical Laboratory at Washington has shown that it has the opposite effect. A similar argument applies to the sun.

Is the magnetic field of the earth due to electric currents flowing inside the earth and around its magnetic axis? To keep such currents flowing permanent electromotive forces are needed. Without continuing electromotive forces their free life is proportional to the conductivity of the medium and the square of the body's radius. "In a globe of copper (at 0° C.) as large as the earth the currents, as Lamb has shown would take about 20,000,000 years to decay in the ratio 10 to 1; while if the globe were as large as the sun the time would be about 200,000,000,000 years. However neither sun nor

earth is held to have as great a conductivity as copper so that if decaying currents bring about the decrease in the earth's magnetic intensity these currents must formerly have been enormously stronger than at present. It may be that currents flow because whatever set them in motion at first is still an effective cause in maintaining them. Sir Joseph Larmor has suggested that the requisite electromotive forces could be produced by a flow of material within the earth that has a component of motion in the meridian planes, but is symmetrical about the axis and likewise about the magnetic equator. Such a circulation might even build up the magnetic field from a small beginning, and ways are known of accounting for such a small initial field. According to Lamb a circulation within the earth would die away very slowly since viscosity is of small influence in large bodies. Observations of sunspots seems to indicate the existence of a streaming of matter in the sun. On the earth the required circulation is not known to occur though, did it exist, it would help to explain continental drift.

"A variety of other explanations of solar or terrestrial magnetism have been proposed, involving rotation as an essential feature. Those based solely on known facts and established physical laws have all failed to explain more than a minute fraction of the observed field." Swann proposes a modification of the electromagnetic equations by introducing small terms depending on the velocity of the electric charge and on its first and second differentials with respect to time. By the proper selection of the form of terms and of numerical factors the solar and terrestrial fields in their actual magnitudes are explained. "The whole procedure is elaborately *ad hoc*, and therefore somewhat unattractive despite the skill with which the theory is developed. One new consequence was inferred from them (the modified equations), namely, that small, rapidly rotating non-magnetic bodies should have a minute but just measurable field. Swann and Longacre have recently succeeded in testing this prediction, which is found to fail." The lecturer is of the opinion that to explain terrestrial magnetism modifications of general physical laws need not be invoked. Making magnetism a property of all rotating bodies is negatived by the secular changes in the earth's field and by the failure on both earth and sun of the magnetic axis to have the same direction as the respective axes of rotation. "Therefore in my opinion cosmical magnetism is only a secondary, though possibly widespread phenomenon, and not a universal fundamental one like gravitation."

In spite of the unsatisfactory state of the theory of the earth's magnetism a study of its phenomena seems likely to add information concerning that little known region, the interior of the earth. An

analysis of the daily variation of the earth's field indicates that the earth is not a uniformly conducting sphere but undergoes a marked change in its composition or state at a layer about 200 miles below the surface. It is computed that from this distance to another 600 miles beneath the surface the resistivity is about 3×10^{12}. This is from 1/400 to 1/4000 of the resistivity of the dry earth or rock constituting the outer portion of the earth.

In addition to the explanation of the general magnetic fields of the earth and of the sun there remains a challenging array of lesser problems. "The solar corona appears to indicate the existence of a magnetic field, probably of low intensity, above the chromosphere. Among the further phenomena of terrestrial magnetism, the chief are the solar and lunar daily variations, and magnetic storms with their associated aurora.

G. F. S.

Tobacco of Reduced Nicotine Content. E. M. BAILEY (*Conn. Agric. Exp. Sta. Bull., 307*, 844–847, 1929) reports analyses of two samples of tobacco prior to and after treatment to reduce its nicotine content. The treatment reduced the nicotine content of one sample from 2.09 per cent. to 0.16 per cent., and of the other sample from 0.98 per cent. to a trace.

J. S. H.

Changes in Tea during Storage. E. M. BAILEY (*Conn. Agric. Exp. Sta. Bull., 307*, 829–831, 1929) reports analyses made on 14 samples of tea in each of three successive years, 1926, 1927, and 1928. The caffeine content remained constant. The tannin content consistently increased as the teas aged. The petroleum ether extract decreased; but the fraction of this extract lost on heating at a temperature of 110° C. showed a slight but consistent increase.

J. S. H.

Color Changes in Animals. SEYMOUR HADWEN of the University of Saskatchewan (*Can. J. Research*, 1929, *1*, 189–200) has made extensive observations on the color changes in the rabbit, *Lepus americanus*, and other animals. The pigment melanin is lacking in the white winter hair, but is plentiful in the dark summer hair, especially in the roots. These changes are attributed to inheritance and not to environment; they are primarily designed to facilitate the retention of heat by the animal in winter and to exclude heat and protect it from ultra-violet light in summer.

J. S. H.

Digestion of Wheat Starch. J. G. MALLOCH of the University of Alberta (*Can. J. Research*, 1929, *1*, 111–147) finds that the diastatic activity of wheat flour depends upon the concentration and activity of the enzyme and upon the resistance of the starch to hydrolysis. Both these factors are influenced by the conditions under which the wheat is grown. The native enzyme of the flour may be inactivated by means of sodium tungstate; when flour has been thus treated, its resistance to digestion or hydrolysis by the enzyme taka-diastase is decreased by continued grinding or by extraction with ether.

J. S. H.

The Naphthoquinone Reaction of Cysteine and Cystine. M. X. SULLIVAN and W. C. HESS (*Public Health Reports*, 1929, *44*, 1599–1608) have studied the groups or compound radicals which must be present in an organic compound of sulphur in order that a red color may develop on the addition of sodium cyanide, 1,2-naphthoquinone-4-sodium sulphonate, sodium sulphite, and sodium hyposulphite in an alkaline medium. They find that the compound must contain three unsubstituted groups; a sulphydrate group (SH), an amino group (NH_2), and a carboxyl group (COOH). These groups occur in cysteine. Cystine is converted into cysteine by the reducing agents used in the test. These two amino acids are the only known compounds which respond to the test and occur, free or combined, in the tissues of animals and plants.

J. S. H.

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